

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C10M 141/10, 141/12, 159/20, 163/00 // (C10M 163/00, 135:02, 135:04, 135:06, 135:18, 137:02, 137:04, 137:10, 139:00, 159:12, 159:20, 159:22, 159:24), C10N 10 :12, 60 :14	A1	(11) International Publication Number: WO 96/37585
		(43) International Publication Date: 28 November 1996 (28.11.96)
(21) International Application Number: PCT/US95/06714 (22) International Filing Date: 26 May 1995 (26.05.95) (71) Applicants: THE LUBRIZOL CORPORATION [US/US]; 29400 Lakeland Boulevard, Wickliffe, OH 44092-2298 (US). ELF ANTAR FRANCE [FR/FR]; Tour Elf, F-92078 Paris-La Défense, Cédex 45 (FR). (72) Inventors: COOK, Susan, P.; 4 Carlisle Avenue, Littleover, Derby DE23 7ET (GB). SCHWIND, James, J.; Charnwood, Church Lane, Doveridge, Derbyshire DE6 5NN (GB). CONSTANS, Bernard; 4, allée des Rameaux, F-69360 Serezin (FR). BOURGOGNON, Henri; 49 bis, avenue du 8-Mai-1945, F-69160 Tassin-la-Demi-Lune (FR). (74) Agent: TRITT, William, C.; Renner, Otto, Boisselle & Sklar, P.L.L., 19th floor, 1621 Euclid Avenue, Cleveland, OH 44115 (US).		(81) Designated States: AU, BR, CA, JP, MX, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: LUBRICANTS WITH MOLYBDENUM CONTAINING COMPOSITIONS AND METHODS OF USING THE SAME		
(57) Abstract This invention relates to a lubricating composition comprising a major amount of an oil of lubricating viscosity and (A) an antiwear improving amount of at least one molybdenum containing composition, and (B) at least one member selected from the group consisting of (i) at least one borated overbased metal salt of an acidic organic compound, provided that (A) and (Bi) are not the same, (ii) a combination of (a) at least one organic polysulfide or at least one ashless dithiocarbamate containing composition and (b) at least one component selected from the group consisting of a metal thiophosphate, a phosphoric acid ester or salt thereof, a phosphorus-containing carboxylic acid, ester, ether, or amide, a borated dispersant, an alkali metal borate, a borated fatty amine, a borated phospholipid, a borate ester, and mixtures thereof, and (iii) a combination of (i) and (ii).		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

Title: LUBRICANTS WITH MOLYBDENUM CONTAINING
COMPOSITIONS AND METHODS OF USING THE SAME

FIELD OF THE INVENTION

This invention relates to a lubricating composition comprising a molybdenum composition which improves the antiwear properties of the lubricant. The invention also relates to methods of lubricating a transmission or differential. These lubricating compositions are particularly useful as manual transmission fluids.

BACKGROUND OF THE INVENTION

Engine, transmission, and gear designs utilize a variety of metallurgy in their designs. In transmissions, often a brass synchronizer ring is used. This brass synchronizer engages with a steel cone to affect changing of the transmission gears. One problem, associated with this design, is brass ring wear. It is therefore desirable to have a lubricant which reduces brass on steel wear.

Often lubricants contain mixtures of additives which are intended to protect the engines, transmissions, and gears against wear and oxidation. Many such mixtures are known to those in the art. However, it would be desirable to have a specific mixture of additives which also provide protection against brass on steel wear.

U.S. Patents 3,541,014 (LeSuer), and 5,143,633 (Gallo et al) describe various molybdenum containing overbased metal salts.

U.S. Patents 3,446,735 (Wiese), 4,289,635 (Schroeck), 4,456,538 (Ripple), 4,692,256 (Umemura et al), 4,704,215 (Hata et al), and 4,846,983 (Ward, Jr.) describe various molybdenum compound and composition either used alone or used in combination with other additives.

SUMMARY OF THE INVENTION

This invention relates to a lubricating composition comprising a major amount of an oil of lubricating viscosity and (A) an antiwear improving amount of at least one molybdenum containing composition, and (B) at least one member selected from the group consisting of (i) at least one borated overbased metal salt of an acidic organic compound, provided that (A) and (Bi) are not the same, (ii) a combination of (a) at least one organic polysulfide or at least one ashless dithiocarbamate containing composition and (b) at least one component selected from the group consisting of a metal thiophosphate,

a phosphoric acid ester or salt thereof, a phosphorus-containing carboxylic acid, ester, ether, or amide, a borated dispersant, an alkali metal borate, a borated fatty amine, a borated phospholipid, a borate ester, and mixtures thereof, and (iii) a combination of (i) and (ii). The lubricating compositions have improved antiwear properties. When the lubricating composition is used in a manual transmission, the amount of brass on steel wear is reduced.

DESCRIPTION OF THE INVENTION

The term "hydrocarbyl" includes hydrocarbon as well as substantially hydrocarbon groups. Substantially hydrocarbon describes groups which contain heteroatom substituents which do not alter the predominantly hydrocarbon nature of the group. Examples of hydrocarbyl groups include the following:

(1) hydrocarbon substituents, i.e., aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, aromatic-, aliphatic- and alicyclic-substituted aromatic substituents and the like as well as cyclic substituents wherein the ring is completed through another portion of the molecule (that is, for example, any two indicated substituents may together form an alicyclic-radical);

(2) substituted hydrocarbon substituents, i.e., those substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent; those skilled in the art will be aware of such groups (e.g., halo (especially chloro and fluoro), hydroxy, mercapto, nitro, nitroso, sulfoxy, etc.);

(3) heteroatom substituents, i.e., substituents which will, while having a predominantly hydrocarbon character within the context of this invention, contain an atom other than carbon present in a ring or chain otherwise composed of carbon atoms (e.g., alkoxy or alkylthio). Suitable heteroatoms will be apparent to those of ordinary skill in the art and include, for example, sulfur, oxygen, nitrogen and such substituents as, e.g., pyridyl, furyl, thienyl, imidazolyl, etc.

In general, no more than about 2, preferably no more than one, hetero substituent will be present for every ten carbon atoms in the hydrocarbyl group. Typically, there will be no such hetero atom substituents in the hydrocarbyl group. Therefore, the hydrocarbyl group is purely hydrocarbon.

In the specification and claims, the term "lubricating composition" refers to the combination of an oil of lubricating viscosity and additives. The percentages by weight are based on the amount of total amount of the additive and the oil of lubricating viscosity.

As described herein, the use of molybdenum containing compositions in combination with specific additives improves the antiwear properties of lubricants, especially brass on steel wear. The molybdenum composition is generally used at a level sufficient to deliver from about 125 up to about 900 ppm, preferably from about 200 up to about 800 ppm, more preferably from about 250 up to about 700 ppm of molybdenum metal to the lubricating composition. Here, as well as elsewhere in the specification, the ratios and range limits may be combined. The molybdenum metal is in an oil soluble or dispersible form. The molybdenum compositions include a molybdenum containing overbased salt of an acidic organic composition, a molybdenum thiocarbamate, and a molybdenum thiophosphate. In one embodiment, the molybdenum composition is other than a molybdenum containing dispersant such as a molybdenum containing succinimide.

Molybdenum Overbased Compositions

In one embodiment, the molybdenum composition is in the form of a molybdenum overbased salt of an acidic organic compound. The molybdenum overbased metal salts are particularly useful in lubricants which require thermal stability. The molybdenum containing overbased salts are characterized by a metal content in excess of that which would be present according to the stoichiometry of the metal and the particular organic compound reacted with the metal. The amount of excess metal is commonly expressed in terms of metal ratio. The term "metal ratio" is the ratio of the total equivalents of the metal to the equivalents of the acidic organic compound. A salt having 4.5 times as much metal as present in a normal salt will have metal excess of 3.5 equivalents per equivalents of organic acid or a ratio of 4.5. The molybdenum containing overbased salts preferably have a metal ratio from about 1.5, or from about 3. The molybdenum containing overbased salts generally have a metal ratio up to about 40, or up to about 30, or up to about 25. In one embodiment, the metal salts have a metal ratio from about 10, preferably from about 12 up to about 40, or up to about 30.

The molybdenum containing overbased salts additionally may contain an alkali or alkaline earth metal. Examples of such metals include sodium, potassium, lithium,

magnesium, calcium, barium, titanium, manganese, cobalt, nickel, copper, and zinc, preferably sodium, potassium, calcium, and magnesium. The alkali or alkaline earth metal may typically be present in an amount from about 2% up to about 20%, or from about 4% up to about 18%, or from about 6 to about 14% by weight of the molybdenum containing overbased salts.

The acidic organic compounds used to prepare the molybdenum containing overbased metal salts are generally selected from the group consisting of sulfonic acids, carboxylic acids, phosphorus acids, phenols, and derivatives thereof. Preferably, the overbased materials are prepared from sulfonic acids, carboxylic acids, or derivatives of these acids, such as esters, anhydrides, etc. The sulfonic acids are preferably mono-, di-, and tri-aliphatic hydrocarbon-substituted aromatic sulfonic acids. The hydrocarbon-substituent may be derived from a polyalkene. The polyalkenes include homopolymers and interpolymers of polymerizable olefin monomers having from 2 up to about 16, preferably from 2 to about 8, more preferably from 2 to about 4 carbon atoms. The olefins may be monoolefins, such as ethylene, propylene, 1-butene, isobutene, and 1-octene; or a polyolefinic monomer, such as 1,3-butadiene and isoprene. In one embodiment, the interpolymer is a homopolymer. An example of a preferred homopolymer is a polybutene, preferably a polybutene in which about 50% of the polymer is derived from isobutylene. The polyalkenes are prepared by conventional procedures.

The polyalkene is generally characterized as containing from at least about 8, or at least about 15, or at least about 20 carbon atoms. The polyalkene generally contains up to about 40 carbon atoms, or up to about 30 carbon atoms. In one embodiment, the polyalkenes have a \bar{M}_n from about 250, or from about 300 up to about 600, or up to about 500, or up to about 400. The abbreviation \bar{M}_n is the conventional symbol representing number average molecular weight. Gel permeation chromatography (GPC) is a method which provides both weight average and number average molecular weights as well as the entire molecular weight distribution of the polymers. For purpose of this invention a series of fractionated polymers of isobutene, polyisobutene, is used as the calibration standard in the GPC.

Examples of sulfonic acids include mahogany sulfonic acids, bright stock sulfonic acids, petroleum sulfonic acids, mono- and polywax-substituted naphthalene sulfonic

acids, saturated, hydroxy-substituted, and unsaturated paraffin wax sulfonic acids, wax-substituted benzene or naphthalene sulfonic acids, tetraisobutylene sulfonic acids, tetra-amylenesulfonic acids, dodecylbenzene sulfonic acids, didodecylbenzene sulfonic acids, dinonylbenzene sulfonic acids, sulfonic acids derived by the treatment of at least one of the above-described polyalkenes (preferably polybutene) with chlorosulfonic acid, and the like.

The sulfonic acids include dodecyl benzene "bottoms" sulfonic acids. Dodecyl benzene bottoms, principally mixtures of mono- and di-dodecyl benzenes, are available as by-products from the manufacture of household detergents. Similar products obtained from alkylation bottoms formed during manufacture of linear alkyl sulfonates (LAS) are also useful in making the sulfonates used in this invention. The production of sulfonic acids is well known to those skilled in the art. See, for example, the article "Sulfonates" in Kirk-Othmer "Encyclopedia of Chemical Technology", Second Edition, Vol. 19, pp. 291 et seq. published by John Wiley & Sons, N.Y. (1969).

In one embodiment, the acidic organic compound may be a carboxylic acid, or derivative thereof. Suitable carboxylic acids include aliphatic, cycloaliphatic, and aromatic mono- and polybasic carboxylic acids. In one embodiment, the carboxylic acid, or derivative thereof, is an aliphatic acid, or derivative thereof, containing from about 8, or from about 12. The carboxylic acid or derivative thereof generally contains up to about 50, or up to about 25 carbon atoms. Illustrative carboxylic acids and derivatives thereof include 2-ethylhexanoic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, behenic acid, octadecyl-substituted adipic acid, stearyl-benzoic acid, polybutenyl substituted succinic acid or anhydride derived from polybutene (\bar{M}_n is from about 200-1500, preferably from about 300-1500, more preferably from about 800-1200), polypropylene substituted succinic acid or anhydride derived from polypropene (\bar{M}_n is from about 200-2000, preferably from about 300-1500, more preferably from about 800-1200), acids formed by oxidation of petrolatum or of hydrocarbon waxes, commercially available mixtures of two or more carboxylic acids, such as tall oil acids and rosin acids, and mixtures of the above acids, and/or their derivatives.

In one embodiment, the carboxylic acid or derivative thereof is a hydrocarbyl-substituted carboxylic acylating agent. The acylating agent includes halides, esters, anhydrides, etc., preferably acid, esters, or anhydrides, more preferably anhydrides.

Preferably the carboxylic acylating agent is a succinic acylating agent. The acylating agent may be derived from a monocarboxylic or a polycarboxylic acylating agent and one or more of the above described polyalkenes. In one embodiment, the polyalkene is characterized by an \bar{M}_n of at least about 400, or at least about 500. Generally, the polyalkene is characterized by an \bar{M}_n from about 500 up to about 5000, or from about 700 up to about 2500, or from about 800 up to about 2000, or from about 900 up to about 1500. In one embodiment, the hydrocarbyl group of the carboxylic acylating agent has a \bar{M}_n from about 400 to about 1200, preferably from about 400 to about 800.

In another embodiment, the hydrocarbyl group is derived from polyalkenes having an \bar{M}_n from about 1300 up to about 5000, and the \bar{M}_w/\bar{M}_n value is from about 1.5 up to about 4, or from about 1.8 to about 3.6, or from about 2.5 to about 3.2. The hydrocarbyl-substituted carboxylic acylating agents are prepared by known procedures.

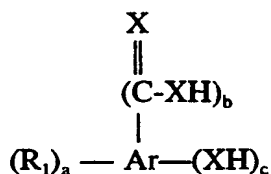
In another embodiment, the acylating agents are prepared by reacting the above described polyalkenes with an excess of maleic anhydride to provide substituted succinic acylating agents wherein the number of succinic groups for each equivalent weight of substituent group is from about 1.3 to about 4.5 succinic groups per equivalent weight of substituent groups. A suitable range is from about 1.4 up to 3.5, or from about 1.5 up to about 2.5 succinic groups per equivalent weight of substituent groups. In this embodiment, the polyalkene has an \bar{M}_n from about 1300 to about 5000. A more preferred range for \bar{M}_n is from about 1500 to about 2800, and a most preferred range of \bar{M}_n is from about 1500 to about 2400.

Carboxylic acids or derivatives thereof (e.g. acylating agents) and their preparation are described in U.S. Patents 3,215,707 (Rense); 3,219,666 (Norman et al); 3,231,587 (Rense); 3,912,764 (Palmer); 4,110,349 (Cohen); and 4,234,435 (Meinhardt et al); and U.K. 1,440,219. The disclosures of these patents are hereby incorporated by reference.

In another embodiment, the acidic organic compound is an alkyloxyalkylene-acetic acid or alkylphenoxy-acetic acid, more preferably alkylpolyoxyalkylene-acetic acid or derivatives thereof. Some specific examples of these compounds include: iso-stearyl-pentaethyleneglycolacetic acid; iso-stearyl-O-(CH₂CH₂O)₃CH₂CO₂Na; lauryl-O-(CH₂CH₂O)_{2.5}CH₂CO₂H; lauryl-O-(CH₂CH₂O)_{3.3}CH₂CO₂H; oleyl-O-(CH₂CH₂O)₄-CH₂CO₂H; lauryl-O-(CH₂CH₂O)_{4.5}CH₂CO₂H; lauryl-O-(CH₂CH₂O)₁₀CH₂CO₂H; lauryl-O-

$(\text{CH}_2\text{CH}_2\text{O})_{16}\text{CH}_2\text{CO}_2\text{H}$; octyl-phenyl-O- $(\text{CH}_2\text{CH}_2\text{O})_8\text{CH}_2\text{CO}_2\text{H}$; octyl-phenyl-O- $(\text{CH}_2\text{CH}_2\text{O})_{19}\text{CH}_2\text{CO}_2\text{H}$; 2-octyldecanyl-O- $(\text{CH}_2\text{CH}_2\text{O})_6\text{CH}_2\text{CO}_2\text{H}$. These acids are available commercially from Sandoz Chemical under the tradename Sandopan acids.

In another embodiment, the acidic organic compound is an aromatic carboxylic acid. A group of useful aromatic carboxylic acids are those of the formula



wherein R_1 is an aliphatic hydrocarbyl group derived from the above-described olefins or polyalkenes, a is a number in the range of 1 to about 4, usually 1 or 2, Ar is an aromatic group, each X is independently sulfur or oxygen, preferably oxygen, b is a number in the range from 1 to about 4, usually from 1 to 2, c is a number in the range of zero to about 4, usually 1 to 2, with the proviso that the sum of a , b , and c does not exceed the number of valences of Ar . Examples of aromatic acids include substituted benzoic, phthalic, and salicylic acids. The R_1 group is a hydrocarbyl group that is directly bonded to the aromatic group Ar . Examples of R_1 groups include substituents derived from the above described polyalkenes.

Ar may be mono- or polynuclear. Mononuclear groups include a phenyl, a pyridyl, or a thienyl. The polynuclear groups may be of the fused type wherein an aromatic nucleus is fused at two points to another nucleus such as found in naphthyl, anthranyl, etc. The polynuclear group can also be of the linked type are linked through bridging linkages such as alkylene, ether, keto, sulfide, disulfide, and polysulfide, containing 3 to about 6 sulfur atoms, linkages. Examples of the aromatic groups include phenyl, phenylene, and naphthalenyl groups.

In one embodiment, the carboxylic acid or derivative thereof is a salicylic acid or derivative thereof. Preferably the salicylic acid or derivative thereof is an aliphatic hydrocarbon-substituted salicylic acid or derivative thereof. The hydrocarbon substituent is generally derived from one or more of the above described polyalkenes.

The above aromatic carboxylic acids are known or can be prepared according to procedures known in the art. Carboxylic acids of the type illustrated by these formulae

and processes for preparing their neutral and basic metal salts are well known and disclosed, for example, in U.S. Patents 2,197,832; 2,197,835; 2,252,662; 2,252,664; 2,714,092; 3,410,798; and 3,595,791. These patents are incorporated by reference for their disclosure of aromatic carboxylic acids, salts thereof and methods of making the same.

In another embodiment, the acidic organic compound is a phosphorus-containing acid, or derivative thereof. The phosphorus-containing acids, or derivatives thereof, include phosphorus acids, such as phosphoric acid or esters; and thiophosphorus acids or esters, including mono and dithiophosphorus acids or esters. In one embodiment, the phosphorus-containing acid is the reaction product of one or more of the above polyalkenes and a phosphorus sulfide. Useful phosphorus sulfides, include phosphorus pentasulfide, phosphorus sesquisulfide, phosphorus heptasulfide and the like. The reaction of the polyalkene and the phosphorus sulfide generally may occur by simply mixing the two at a temperature above 80°C, usually between 100°C and 300°C. Generally, the products have a phosphorus content from about 0.05% to about 10%, preferably from about 0.1% to about 5%. The relative proportions of the phosphorizing agent to the olefin polymer is generally from 0.1 part to 50 parts of the phosphorus sulfide per 100 parts of the polyalkene. The phosphorus-containing acids are described in U.S. Patent 3,232,883 issued to LeSuer. This reference is herein incorporated by reference for its disclosure to the phosphorus-containing acids and methods for preparing the same.

In another embodiment, the acidic organic compound is a phenol. The phenols may be represented by the formula $(R_1)_a\text{-Ar-(OH)}_b$, wherein R_1 is defined above for the aromatic carboxylic acids; Ar is an aromatic group, as defined above; a and b are independently numbers of at least one, the sum of a and b being in the range of two up to the total number of displaceable hydrogens on the aromatic nucleus or nuclei of Ar. Preferably, a and b are independently numbers in the range of 1 to about 4, or to about 2. In one embodiment, R_1 and a are such that there is an average of at least about 8 aliphatic carbon atoms provided by the R_1 groups for each phenol compound.

In another embodiment, the molybdenum containing overbased metal salts are borated molybdenum containing overbased metal salts. The molybdenum containing borated overbased metal salts are prepared by reacting one of the below described borated

overbased metal salts with a molybdenum containing anion. Alternatively, the molybdenum containing borated overbased metal salts may be prepared by incorporating the boron compound into the initial reaction mixture used to make the molybdenum containing metal salts.

Preparation of the Molybdenum Containing Overbased Composition

In one embodiment, the molybdenum containing overbased compositions are prepared by reacting molybdenum containing anions with an alkali or alkaline earth metal overbased salt of an acidic organic compound. The alkali or alkaline earth metal salts are prepared by reacting an acidic material, described below (typically carbon dioxide), with a mixture comprising an acidic organic compound, such as those described above, a reaction medium comprising at least one inert, organic solvent for the organic material, a stoichiometric excess of the alkali or alkaline earth basic metal compound, typically a metal hydroxide or oxide, and a promoter, including alcoholic and phenolic promoters, such as alcohols having about one to about 12 carbon atoms (such as methanol, ethanol, amyl alcohol, octanol, isopropanol, and mixtures of these), and alkylated phenols (such as heptylphenols, octylphenols, and nonylphenols).

Illustrative of alkali or alkaline earth basic metal compounds include hydroxides, oxides, alkoxides (typically those in which the alkoxy group contains up to 10 and preferably up to 7 carbon atoms), hydrides and amides of alkali or alkaline earth metals. Useful basic metal compounds include lithium hydroxide, sodium hydroxide, potassium hydroxide, magnesium oxide, calcium hydroxide, calcium oxide, and barium hydroxide. The alkali and alkaline earth metal salts and methods of making the same are described in U.S. Patent 4,627,928. This patent is hereby incorporated by reference for such disclosure. A comprehensive discussion of suitable promoters is found in U.S. Patents 2,777,874; 2,695,910; 2,616,904; 3,384,586; and 3,492,231. These patents are incorporated by reference for their disclosure of promoters.

The temperature at which the acidic material is contacted with the remainder of the reaction mass depends to a large measure upon the promoting agent used. With a phenolic promoter, the temperature usually ranges from about 80°C to about 300°C, and preferably from about 100°C to about 200°C. When an alcohol or mercaptan is used as the promoting agent, the temperature usually will not exceed the reflux temperature of the reaction mixture.

Acidic materials, which are reacted with the mixture of the acidic organic compound, the promoter, the metal compound and the reactive medium, are also disclosed in the above cited patents, for example, U.S. Patent 2,616,904. Included within the known group of useful acidic materials are formic acid, acetic acid, nitric acid, boric acid, sulfuric acid, hydrochloric acid, hydrobromic acid, carbamic acid, substituted carbamic acids, etc. Acetic acid is a very useful acidic material. Inorganic acidic compounds such as HCl, SO₂, SO₃, CO₂, H₂S, N₂O₃, etc., may also be employed as the acidic materials. Preferred acidic materials are SO₂, SO₃, carbon dioxide and acetic acid, more preferably carbon dioxide.

The methods for preparing the overbased materials are well known in the prior art and are disclosed, for example, in the following U.S. Patent Nos.: 2,616,904; 2,616,905; 2,616,906; 3,242,080; 3,250,710; 3,256,186; 3,274,135; 3,492,231; and 4,230,586. These patents disclose processes, materials which can be overbased, suitable metal bases, promoters, and acidic materials. These patents are incorporated herein by reference for these disclosures. Other descriptions of basic sulfonate salts and techniques for making them can be found in the following U.S. Patents: 2,174,110; 2,202,781; 2,239,974; 2,319,121; 2,337,552; 3,488,284; 3,595,790; and 3,798,012. These are hereby incorporated by reference for their disclosures in this regard.

As described above the alkali or alkaline earth overbased compositions may be reacted with molybdenum containing anions to form the molybdenum containing overbased metal salts of acidic organic compounds. The molybdenum anions are delivered as molybdic acid or ammonium or alkali metal salts of molybdic acid including (NH₄)₆ Mo₇ O₂₄, (NH₄)₂ Mo₂ O₇ and various hydrates, such as (NH₄)₆ Mo₇ O₂₄ 4H₂O. In one embodiment, the reaction is facilitated by the use of a peptizing agent. Peptizing agents include one or more of the dispersants described herein. This process and the molybdenum containing overbased compositions are described in U.S. Patent 3,541,014 (LeSuer). This patent is incorporated by reference for this disclosure.

In another embodiment, the molybdenum containing overbased compositions are prepared by reacting the components used in the overbasing process in the presence of at least one organic molybdenum complex. The molybdenum containing organic complex is preferably an amine-molybdenum complex, which are typically prepared by a reaction of an acidic and organic molybdenum compound with an amine. The molybdenum

compounds include molybdic acid, alkali metal molybdates, sodium hydrogen molybdate, ammonium molybdate, MoOCl_4 , and molybdenum trioxide. Sodium molybdate and ammonium molybdate are preferred. The amine-molybdenum complex is in general prepared in an aqueous medium. The amine is added to an aqueous solution of an inorganic molybdenum compound. The reaction mixture is kept at a temperature between about 20° and about 100° C, preferably between about 50° and about 90° C, for about 0.5 to about 3 hours after the addition of the amine. The amount of acid necessary to neutralize the reaction mixture is added before or after the introduction of the amine. A strong mineral acid is used, preferably sulfuric acid. The amine-molybdenum complex precipitates. It is recovered by filtering off, washed with water and dried, if appropriate. The complex has a solid or pasty appearance, depending on the type of amine used. Its color varies from white to blue. It is virtually insoluble or very sparingly soluble in hydrocarbons.

The atomic ratio of nitrogen to molybdenum in the complex is in general from about 0.25 to about 4, preferably from about 0.5 to about 2. The molybdenum content of the complex varies depending on the nature of the amine used: it is between about 10% and about 45%. Among the organic molybdenum complexes, the complexes with oxygen-containing compounds may also be used. The 1,2-, 1,3- and 1,4-glycols are very particularly suitable. Ethylene glycol and propylene glycol are preferably used. Amongst the polyols, are glycerol and trimethylolpropane.

Some amines, or polyamines which are alkoxyated, preferably with ethylene oxide or propylene oxide, are also suitable. The derivatives of diethanolamine or of triethanolamine may be mentioned.

The preparation of the molybdenum containing overbased compositions can be carried out by heating the oxygen-containing compound at about 90° - 100° C in the presence of a molybdenum compound, such as ammonium molybdate. The water produced by the reaction is removed using a stream of nitrogen. The molybdenum content of the complexes obtained varies between about 7% and about 50% by weight, depending on the degree to which unreacted oxygen-containing compound has been removed.

The organic molybdenum complex can be sulfurized, for example, by the action of hydrogen sulfide (H_2S) on a suspension of the complex in an aromatic solvent such as

xylene or toluene, at a temperature of between about 40°C and about 100°C. From the introduction of hydrogen sulfide, the color of the suspension changes from blue-green to orange, and then to red. The amount of hydrogen sulfide introduced is such that the atomic ratio of sulfur to molybdenum is between about 1 and about 3.

The overbased products containing molybdenum, obtained according to the invention, are clear and stable and colored brown in the case of the sulfonates, deep green in the case of the phenolates and black in the case of the salicylates. The color is generally red for the overbased detergents in the presence of a sulfurized complex. The proportion of molybdenum incorporated in the additive is close to 100%, higher than the proportions obtained during incorporation of inorganic molybdenum derivatives. The additive contains from about 0.1% to about 10% by weight, preferably from about 1% to about 4% of molybdenum. The overbased additives according to the invention are soluble or dispersible in hydrocarbons. The molybdenum containing overbased salts prepared with molybdenum amine complexes are described in U.S. Patent 5,143,633. This patent is incorporated by reference for its description of the molybdenum containing overbased salts and methods of making the same.

The following Examples relate to molybdenum containing overbased compositions and methods of making the same. In the Examples, as well as elsewhere in the specification and claims, unless the context indicates otherwise, the parts and percentages are by weight, the temperature is degrees Celsius, and the pressure is atmospheric. In the examples the basicity of these overbased additives is characterized by their neutralization number or AV (alkali value) is expressed in mg of KOH per gram of product. It is determined by titration with aid of a strong acid in accordance with the standard ASTM D-2896.

Example M-1

(a) A solution of 41.17 g of sodium molybdate $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ in 100 ml of water is prepared in a reactor fitted with a temperature control and a stirrer device. The mixture is acidified by adding 55.6 g of 30% H_2SO_4 and then heated to 60° C. This is followed by the addition of 21 g of Dinoram C from CECA SA. Dinoram C corresponds to the formula $\text{R-N-H}-(\text{CH}_2)_3\text{-NH}_2$, where R is a mixture of straight-chain saturated alkyl radicals containing 60% of C_{12} , 20% of C_{14} , 10% of C_{16} and 5% of C_{18} . The blue precipitate is recovered by filtering off and then washing with water and with methanol

before drying. Finally, 47.1 g of blue solid containing 32.6% of molybdenum and 4.4% of nitrogen are recovered.

(b) A reaction vessel is charged with 520 ml of xylene and 30 grams of the Dinoram C/molybdenum complex from above. The mixture is stirred. Then, 131.8 g of alkylxylenesulfonic acid having C_{16-18} straight-chain alkyl chain and a molecular weight of 430 and containing 96% of active substance, 168 g of diluent oil 100 Neutral solvent, 113.24 g of slaked lime of 96% purity and 48 ml of methanol are added to the mixture. After neutralization of the sulfonic acid with the lime, which, if appropriate, can be carried out by heating the reaction mixture at 60°C for 30 minutes, 55.2 g of carbon dioxide gas are then introduced into the mixture which is kept at a temperature of 42°C.

After carbonation and removal of water and methanol under partial vacuum, the solid residues are removed by centrifuging. After evaporating off the solvent, 448 g of molybdenum-containing superbasic sulfonate are recovered; neutralization number = 300, its calcium contents is 11.7% and its molybdenum content 2.17%. It is stable on dilution in lubricant oils.

Example M-2

(a) A dispersion of 20 g of the complex prepared in Example M-1 in 200 ml of xylene is prepared in a 250 ml reactor fitted with a temperature control, a stirrer and a gas bubbling system. 6.7 g of H_2S are injected into the dispersion kept at 80°C; the deep red solid collected after removal of the solvent contains 28.4% of molybdenum, 3.8% of nitrogen and 23.7% of sulfur.

(b) The procedure is as in Example M-1, but 28 g of sulphurized Dinoram C/molybdenum complex (Example M-2(a)) are suspended in 520 ml of xylene, this being carried out before the introduction of the other reactants. The sequence of operations is identical to that of Example M-1 except that the residues are removed by centrifuging. A molybdenum-containing superbasic sulphonate is collected; AV = 304. The molybdenum, sulphur and calcium contents are, respectively, 1.63, 3.4 and 11.7%. The product obtained has a brown-red color and it is stable on dilution in lubricant oils.

Example M-3

(a) A 2-ethylhexylamine/molybdenum complex is prepared as follows: The procedure is as in Example M-1 but 9.9 g of 98% 2-ethylhexylamine are added at 60°C before heating and acidification and are introduced in the course of 20 minutes into an

aqueous solution containing 15.44 g of sodium molybdate and kept at 60° C. After heating at 60° C. for 45 minutes, the mixture is acidified with 23.1 g of 30% sulfuric acid, before washing and drying the product. The latter is in the form of a white solid containing 36.8% of molybdenum and 4.38% of nitrogen.

5 (b) The procedure is as in Example M-1, but 28 g of the 2-ethylhexylamine complex prepared in Example M-3(a) are suspended in 520 ml of xylene before the introduction of the other reactants. The procedure is the same as in Example M-1 except that the residues are removed by centrifuging. A brown product of AV = 353 is collected. The calcium and molybdenum contents are, respectively, 12.2 and 1.97%.
0 The stability on dilution in lubricant oils is perfect.

Example M-4

The procedure is as in Example M-1(b), but 600 milliliters of xylene, 132 grams of didodecylbenzenesulfonic acid having a molecular weight of 520 and containing 70% of active substance 30 grams of the complex prepared in Example M-1(a), 104 grams of
5 slaked lime, 52 milliliters of methanol, 4.4 milliliters of ammonia and 90 grams of diluent oil are introduced successively into the reactor. The product collected is brown, clear and stable in oils. The calcium and molybdenum contents are, respectively, 10 and 2.35%.

The procedure is as in Example M-1, but 30 grams of the complex prepared in
10 Example M-1(a) are introduced into 520 milliliters of toluene before the addition of other reactants. The sequence of operations is identical to that of Example 1 except that 52.7 grams of CO₂ are introduced during the carbonation. After centrifuging, 448 grams of molybdenum-containing superbaseic sulfonate are recovered. AV=298. The calcium and molybdenum contents are , respectively, 11.7% and 2.1%.

Example M-5

The procedure is as in Example M-4, but after filtration on diatomaceous earth, 440 grams of molybdenum-containing overbased sulfonate of AV=292 are recovered.

Example M-4

(a) Preparation of barium overbased amine-formaldehyde condensate: A
10 reaction vessel is charged with 1000 parts of N-octadecyl propylenediamine, 490 parts of mineral oil, 32 parts of calcium oxide, and 143 parts of water at about 44°C and slowly heated to 102°C under reflux conditions over a one hour period. While

maintaining the mixture at 100°-105°C, 303 parts of paraformaldehyde are added to the reaction mixture over three hours. The temperature is maintained for one hour, then the temperature is increased to 150°C over two and one half hours. Distillate (278 parts) is removed and the residue is filtered.

A separate reaction vessel is charged with 197 parts of mineral oil and 119 parts of heptylphenol. The mixture is heated to 93-99°C where barium hydroxide monohydrate (465 parts) is added over four hours. The reaction temperature is then increased to 150°C where 149 parts of the above amine-formaldehyde product (Example M-3(a)) is added over one half hour. Carbon dioxide is blown subsurface into the mixture at a rate of 15 parts per hour for seven hours at 150°C. Additional mineral oil (100 parts) is added to the mixture and the mixture is blown with nitrogen subsurface for two hours at 150°C. The water content of the mixture is reduced to 0.3%. The residue is filtered through diatomaceous earth and the filtrate is the desired product. The product has 36% mineral oil and 30.8% barium.

(b) An aqueous mixture of ammonium paramolybdate tetrahydrate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, is prepared by mixing 411 grams thereof with 300 grams of water and maintaining the temperature of the mixture at about 60° C. Four 100-gram portions of this mixture are added to 457 grams of the above barium overbased amine aldehyde condensate (Example M-5(a)) over a 3.5 hour period while maintaining the temperature of the reaction mass at about 95° C. This results in a molar ratio of barium to molybdenum of 3:1. During the addition of the aqueous mixture, ammonia and carbon dioxide are evolved. Thereafter, volatiles are removed from the reaction mass by heating to 150° C, while blowing with nitrogen. The residue is filtered yielding 550 grams of an oil solution on the desired molybdenum-containing complex. Analysis of the product establishes that about 65% of the molybdenum employed in the reaction is retained in the molybdenum-containing complex thus produced.

Example M-5

(A) A mixture of 44 parts (all parts refer to parts by weight) of the product of Example M-4(b), 10 parts mineral oil, and 24 parts of the reaction product of polyisobutene ($\bar{M}_n = 750$)-substituted succinic anhydride with a commercial mixture of polyethylene polyamines having an average composition corresponding to that of tetraethylene pentamine (reacted in a ratio of equivalents of 1:1 according to the

procedure of U.S. patent 3,172,892, e.g., Example 12 thereof) is prepared and heated to about 75° C. over a 1.5 hour period. The weight ratio of peptizing agent to overbased material is 5:95. To this solution there is added 520 parts of an aqueous ammonium molybdate solution previously prepared by mixing 265 parts by weight of water and 265 parts by weight of a commercial ammonium molybdate (ammonium dimolybdate sold by the Climax Molybdenum Company having a composition corresponding to the formula $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$ containing about 56.5% by weight molybdenum) over a 1.5 hour period while maintaining a temperature at about 70-80° C. resulting in a molar ratio of barium to molybdenum of 1:1.53. The resulting reaction mass is heated under reflux conditions at about 150° C. for about 8.8 hours. Subsequently, the mixture is blown with nitrogen at about 5 parts per hour while maintaining the temperature at about 150° C. for an additional 1.3 hours. The nitrogen blowing is thereafter ceased, the mixture is maintained at about 150° C. for an additional hour and the entire reaction mass is filtered. The filtrate contains the desired molybdenum-containing complex and is characterized by having 19.67% by weight molybdenum and 21.81% by weight barium.

(B) To a mixture of 2.285 grams of the overbased product of Example M-4(b) and 125 grams of the peptizing agent referred to above (Example M-5(a)), there is added slowly over three hours 2600 grams of an aqueous solution of ammonium paramolybdate tetrahydrate (prepared by mixing 1300 grams of the molybdate and 1300 grams of water) while maintaining a temperature slightly above 70° C. The weight ratio of peptizing agent to overbased product is 5:95 and the barium to molybdenum molar ratio of 1:1.47. Ammonia, carbon dioxide, and water are evolved during the ensuing reaction. Thereafter, nitrogen is bubbled through the reaction mass to remove water and gases during which time the product is heated to 170° C for four hours. Then a commercial filter aid is added and the mass is filtered. The filtrate weighs 2.710 grams and contains 20.2% by weight molybdenum, 21.6% by weight barium, and 25.3% by weight oil.

Molybdenum Containing Thiocarbamates and Thiophosphates

As described above, the molybdenum composition may be a molybdenum containing thiocarbamate or thiophosphate. The molybdenum compositions include molybdenum oxysulfide thiocarbamates and molybdenum oxysulfide thiophosphates. Thiocarbamates and their preparation are described below. Molybdenum containing thiocarbamates, including dithiocarbamates are known to those in the art. These

materials are described in U.S. Patents 4,098,705, 4,259,194, 4,259,195, 4,265,773, 4,272,387, 4,282,822, 4,283,295, 4,369,119, 4,395,423, and 4,402,840. These patents are incorporated by reference for their disclosure of molybdenum containing carbamates and methods of making the same. Examples of commercially available molybdenum containing thiocarbamates include Sakura Lube 500 (20% molybdenum dithiocarbamate from Sakura Chemical), and Molyvan 807 (5% molybdenum dithiocarbamate from Vanderbilt Chemical). The inventors have discovered that the molybdenum containing dithiocarbamates are useful in lubricating compositions which require thermal stability. The level of molybdenum preferred for molybdenum containing dithiocarbamates is from about 200 to about 800, preferably from about 250 to about 600, more preferably from about 300 to about 500 ppm.

In another embodiment, the molybdenum containing composition is a molybdenum thiophosphate. The molybdenum salts of thiophosphorus acids are known those in the art. The thiophosphorus acids, including dithiophosphoric acids, are described below. Molybdenum salts and the methods of their preparation are described in U.S. Patent 3,223,625, 3,256,184, 3,400,140, 3,494,866, 3,840,463, and 4,156,099. These patents are hereby incorporated by reference for such disclosure.

Borated Overbased Salts

In one embodiment, the molybdenum containing compositions are used in combination with borated overbased metal salts. The borated overbased metal salts are prepared by reacting a boron compound with one or more of the above overbased metal salts, or by using boric acid to overbase an acidic organic compound. The borated overbased metal salts are generally used in an amount from about 0.1% up to about 5%, or from about 0.5% up to about 3%, or from about 0.5% up to about 2% by weight of the lubricating compositions.

Boron compounds include boron oxide, boron oxide hydrate, boron trioxide, boron trifluoride, boron tribromide, boron trichloride, boron acid such as boric acid, tetraboric acid and metaboric acid, boron hydrides, boron amides and various esters of boron acids. The boron esters are preferably lower alkyl (1-7 carbon atoms) esters of boric acid. A preferred boron compound is boric acid. Generally, the overbased salts are reacted with a boron compound at about 50°C to about 250°C, preferably from about 100°C to about 200°C. The overbased salts are generally reacted with a boron compound in amounts to

provide at least about 0.5%, or at least about 1% by weight boron to the composition. The overbased metal salt is generally reacted with a boron compound in an amount to provide up to about 5%, or up to about 4%, or up to about 3% by weight boron to the composition.

Borated overbased compositions, lubricating compositions containing the same and methods of preparing borated overbased compositions are found in U.S. Patent 4,744,920, issued to Fischer et al; U.S. Patent 4,792,410 issued to Schwind et al and PCT Publication WO 88/03144. The disclosures relating to the above are hereby incorporated by reference.

In another embodiment, the borated overbased metal salts are prepared by reacting the acidic organic compound with a basic metal salts in the presence of a boron compound. The metals include transition metals, such as zinc, copper, and cadmium. These borated overbased compositions and methods of their preparation are described in U.S. Patent 5,064,545 (Steckel). This patent is incorporated by reference for such disclosure.

The following examples relate to borated overbased metal salts.

Example B-1

(a) A mixture of 853 grams of methyl alcohol, 410 grams of blend oil, 54 grams of sodium hydroxide, and a neutralizing amount of additional sodium hydroxide is prepared. The amount of the latter addition of sodium hydroxide is dependent upon the acid number of the subsequently added sulfonic acid. The temperature of the mixture is adjusted to 49°C. A mixture (1070 grams) of straight chain dialkyl benzene sulfonic acid ($\bar{M}_w=430$) and blend oil (42% by weight active content) is added while maintaining the temperature at 49-57°C. Polyisobutenyl ($\bar{M}_n=950$)-substituted succinic anhydride (145 grams) is added to the reaction vessel. Then, 838 grams of sodium hydroxide (838 grams) are added and the temperature is adjusted to 71°C. The reaction mixture is blown with 460 grams of carbon dioxide. The mixture is flash stripped to 149°C, and filtered to clarity to provide the desired product. The product is an overbased sodium sulfonate having a base number (bromophenol blue) of 440, a metal content of 19.4% by weight, a metal ratio of 20, a sulfate ash content of 58% by weight, and a sulfur content of 1.3% by weight.

(b) A reaction vessel is charged with 1000 grams of the above overbased sodium salt (Example B-1(a)), 0.13 gram of an antifoaming agent (kerosene solution of Dow Corning 200 Fluid having a viscosity of 1000 cSt at 25°C), and 133 grams of blend oil is heated to 74-79°C with stirring. Then, 486 grams of boric acid are added to the reaction mixture. The reaction mixture is heated to 121°C to liberate water of reaction and 40-50% by weight of the CO₂ contained in the above overbased sodium salt. The reaction mixture is heated to 154-160°C and maintained at that temperature until the free and total water content is reduced to 0.3% by weight or less and approximately 1-2% by weight, respectively. The reaction product is cooled to room temperature and filtered.

Example B-2

(a) A mixture of 1000 grams of a primarily branched chain monoalkyl benzene sulfonic acid ($\bar{M}_w=500$), 771 grams of o-xylene, and 75.2 grams of polyisobutenyl ($\bar{M}_n=950$) succinic anhydride is prepared and the temperature is adjusted to 46°C. Magnesium oxide (87.3 grams), acetic acid (35.8 grams), methyl alcohol (31.4 grams), and water (59 grams) are added sequentially to the reaction mixture. The reaction mixture is blown with 77.3 grams of carbon dioxide at a temperature of 49-54°C. Then, 87.3 grams of magnesium oxide, 31.4 grams of methyl alcohol and 59 grams of water are added, and the reaction mixture is blown with 77.3 grams of carbon dioxide at 49-54°C. The foregoing steps of magnesium oxide, methyl alcohol and water addition, followed by carbon dioxide blowing are repeated once. O-xylene, methyl alcohol and water are removed from the reaction mixture using atmospheric and vacuum flash stripping. The reaction mixture is cooled and filtered to clarity. The product is an overbased magnesium sulfonate having a base number (bromophenol blue) of 400, a metal content of 9.3% by weight, a metal ratio 14.7, a sulfate ash content of 46.0%, and a sulfur content of 1.6% by weight.

(b) A reaction vessel is charged with 1000 grams of the above overbased magnesium salt (Example B-2(a)) and 181 grams of diluent oil is heated to 79°C. Then, 300 grams of boric acid are added to the reaction mixture and the mixture is heated to 124°C over a period of 8 hours. The reaction mixture is maintained at 121-127°C for 2-3 hours until the magnesium content remains constant at 6.8% by weight. A nitrogen sparge is started and the reaction mixture is heated to 149°C to remove water until the

water content is 3% by weight or less. The reaction mixture is filtered to provide the desired product.

The molybdenum containing composition may be used in combination with (i) an organic polysulfide or an ashless dithiocarbamate composition and (ii) a phosphorus or boron extreme pressure agent. The organic polysulfide or the ashless dithiocarbamate composition are generally used in an amount from about 0.5% up to about 5%, or from about 1% up to about 4%, or from about 2% up to about 3.5% by weight of the lubricating composition.

Organic Polysulfide or Ashless Dithiocarbamate Containing Composition

The organic polysulfide is characterized as having sulfide linkages having from at least 2 to about 10 sulfur atoms, preferably 2 to about 6 sulfur atoms, more preferably 2 to about 4 sulfur atoms. The organic polysulfides are generally di-, tri- or tetrasulfide compositions with trisulfide compositions preferred.

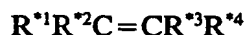
The organic polysulfides of the present invention provide from about 1% to about 3% sulfur to the lubricating compositions. Generally, the organic polysulfides contain from about 10% to about 60% sulfur, preferably from about 20% to about 50%, and more preferably from about 35% to about 45% sulfur. Materials which may be sulfurized to form the organic polysulfides include oils, fatty acids or esters, or olefins, or polyolefins. These materials are sulfurized by their reaction with sulfurizing agents, such as elemental sulfur, sulfur halides, combinations of sulfur with hydrogen sulfide, etc.

Oils which may be sulfurized are natural or synthetic oils including mineral oils, lard oil, carboxylate esters derived from aliphatic alcohols and fatty acids or aliphatic carboxylic acids (e.g., myristyl oleate and oleyl oleate), sperm whale oil and synthetic sperm whale oil substitutes and synthetic unsaturated esters or glycerides.

Fatty acids generally contain from about 4 up to about 30, or from about 8 up to about 24 carbon atoms such as palmitoleic, oleic, ricinoleic, linoleic, oleostearic, etc. Sulfurized fatty acid esters are prepared from mixed unsaturated fatty acid esters such as those obtained from animal fats and vegetable oils and including tall oil, linseed oil, rape oil, fish oil, sperm oil, etc.

The olefinic compounds which may be sulfurized contain at least one olefinic double bond. The double bond is defined as a non-aromatic double bond; that is, one

connecting two aliphatic carbon atoms. In its broadest sense, the olefin may be defined by the formula



wherein each of R^1 , R^2 , R^3 and R^4 is hydrogen or an organic group. In general, the R groups in the above formula which are not hydrogen may be satisfied by such groups as $-C(R^5)_3$, $-COOR^5$, $-CON(R^5)_2$, $-COON(R^5)_4$, $-COOM$, $-CN$, $-X$, $-YR^5$ or $-Ar$, wherein: each R^5 is independently hydrogen, alkyl, alkenyl, aryl, substituted alkyl, substituted alkenyl or substituted aryl, with the proviso that any two R^5 groups can be alkylene or substituted alkylene whereby a ring of up to about 12 carbon atoms is formed; M is one equivalent of a metal cation (preferably Group I or II, e.g., sodium, potassium, barium, calcium); X is halogen (e.g., chloro, bromo, or iodo); Y is oxygen or divalent sulfur; Ar is an aryl or substituted aryl group of up to about 12 carbon atoms. Any two of R^1 , R^2 , R^3 and R^4 may also together form an alkylene or substituted alkylene group; i.e., the olefinic compound may be alicyclic.

The olefinic compound is usually one in which each R^* group which is not hydrogen is independently alkyl, alkenyl or aryl group. Monoolefinic and diolefinic compounds, particularly the former, are preferred, and especially terminal monoolefinic hydrocarbons; that is, those compounds in which R^3 and R^4 are hydrogen and R^1 and R^2 are alkyl or aryl, especially alkyl (that is, the olefin is aliphatic) having 1 to about 30, preferably 1 to about 16, more preferably 1 to about 8, and more preferably 1 to about 4 carbon atoms. Olefinic compounds having about 3 to about 30 and especially about 3 to about 16 (most often less than about 9) carbon atoms are particularly desirable.

Isobutene, propylene and their dimers, trimers and tetramers, and mixtures thereof are especially preferred olefinic compounds. Of these compounds, isobutylene and diisobutylene are particularly desirable because of their availability and the particularly high sulfur containing compositions which can be prepared therefrom.

In one preferred embodiment, the organic polysulfide comprise sulfurized olefins, where the olefins are described above. For example, organic polysulfides may be prepared by the sulfochlorination of olefins containing four or more carbon atoms and further treatment with inorganic higher polysulfides according to U.S. Patent 2,708,199.

In one embodiment, sulfurized olefins are produced by (1) reacting sulfur monochloride with a stoichiometric excess of a low carbon atom number olefin, (2) treat-

ing the resulting product with an alkali metal sulfide in the presence of free sulfur in a mole ratio of no less than 2:1 in an alcohol-water solvent, and (3) reacting that product with an inorganic base. This procedure is described in U.S. Patent 3,471,404, and the disclosure of U.S. Patent 3,471,404 is hereby incorporated by reference for its discussion of this procedure for preparing sulfurized olefins and the sulfurized olefins thus produced. Generally, the olefin reactant contains from about 2 to about 5 carbon atoms and examples include ethylene, propylene, butylene, isobutylene, amylene, etc.

The sulfurized olefins which are useful in the compositions of the present invention also may be prepared by the reaction, under superatmospheric pressure, of olefinic compounds with a mixture of sulfur and hydrogen sulfide in the presence of a catalyst, followed by removal of low boiling materials. This procedure for preparing sulfurized compositions which are useful in the present invention is described in U.S. Patent 4,191,659, the disclosure of which is hereby incorporated by reference for its description of the preparation of useful sulfurized compositions.

In one embodiment, the organic polysulfide may be prepared by reaction of a mercaptan and sulfur in the presence of a catalyst, such as magnesium oxide, alumina catalyst. The mercaptans used to make the polysulfide may be hydrocarbyl mercaptans, such as those represented by the formula $R-S-H$, wherein R is a hydrocarbyl group as defined above. In one embodiment, R is an alkyl, an alkenyl, cycloalkyl, or cycloalkenyl group. R may also be a haloalkyl, hydroxyalkyl, or hydroxyalkyl substituted (e.g. hydroxymethyl, hydroxyethyl, etc.) aliphatic groups. R generally contains from about 2 to about 30 carbon atoms, or from about 2 to about 24, or from about 3 to about 18 carbon atoms. Examples include butyl mercaptan, amyl mercaptan, hexyl mercaptan, octyl mercaptan, 6-hydroxymethyloctanethiol, nonyl mercaptan, decyl mercaptan, 10-amino-dodecanethiol, dodecyl mercaptan, 10-hydroxymethyl-tetradecanethiol, and tetradecyl mercaptan. These organic polysulfides and processes for making them are disclosed in U.S. Patent 4,564,709, issued to Koyama et al and U.S. Patent 5,146,000, issued to Ozbalik. These patents are incorporated by reference for such disclosure.

The following example relates to organic polysulfides.

Example S-1

Sulfur (526 parts, 16.4 moles) is charged to a jacketed, high-pressure reactor which is fitted with an agitator and internal cooling coils. Refrigerated brine is circulated

through the coils to cool the reactor prior to the introduction of the gaseous reactants. After sealing the reactor, evacuating to about 2 torr and cooling, 920 parts (16.4 moles) of isobutene and 279 parts (8.2 moles) of hydrogen sulfide are charged to the reactor. The reactor is heated using steam in the external jacket, to a temperature of about 182°C over about 1.5 hours. A maximum pressure of 1350 psig is reached at about 168°C during this heat-up. Prior to reaching the peak reaction temperature, the pressure starts to decrease and continues to decrease steadily as the gaseous reactants are consumed. After about 10 hours at a reaction temperature of about 182°C, the pressure is 310-340 psig and the rate of pressure change is about 5-10 psig per hour. The unreacted hydrogen sulfide and isobutene are vented to a recovery system. After the pressure in the reactor has decreased to atmospheric, the sulfurized mixture is recovered as a liquid.

Example S-2

Sulfur monochloride (2025 grams, 15.0 moles) is heated to 45°C. Through a sub-surface gas sparge, 1468 grams (26.2 moles) of isobutylene gas are fed into the reactor over a 5-hour period. The temperature is maintained between 45-50°C. At the end of the sparging, the reaction mixture increases in weight of 1352 grams. In a separate reaction vessel are added 2150 grams (16.5 moles) of 60% flake sodium sulfide, 240 grams (7.5 moles) sulfur, and a solution of 420 ml. of isopropanol in 4000 ml. of water. The contents are heated to 40°C. The adduct of the sulfur monochloride and isobutylene previously prepared is added over a three-quarter hour period while permitting the temperature to rise to 75°C. The reaction mixture is heated to reflux for 6 hours, and afterward the mixture is permitted to form into separate layers. The lower aqueous layer is discarded. The upper organic layer is mixed with two liters of 10% aqueous sodium hydroxide, and the mixture is heated to reflux for 6 hours. The organic layer is again removed and washed with one liter of water. The washed product is dried by heating at 90°C and 30 mm. Hg. pressure for 30 minutes. The residue is filtered through diatomaceous earth filter aid to give 2070 grams of a clear yellow-orange liquid.

The ashless dithiocarbamate compositions include reaction products of a dithiocarbamic acid or salt and an unsaturated amide, carboxylic acid, anhydride, or ester, or ether, alkylene-coupled dithiocarbamate, and bis(S-alkyldithiocarbamoyl) disulfides. The dithiocarbamate compounds (A) may be prepared by reacting a dithiocarbamic acid or salt with an unsaturated compound. The dithiocarbamate compositions may also be prepared.

by simultaneously reacting an amine, carbon disulfide and an unsaturated compound. Generally, the reaction occurs at a temperature from about 25°C to about 125°C, or from about 50°C to about 100°C. U. S. Patents 4,758,362 and 4,997,969 describe dithiocarbamate compositions and methods of making the same. These patents are hereby
5 incorporated by reference for their disclosure of dithiocarbamate compositions and method of making the same.

The dithiocarbamic acid or salt used to prepare the dithiocarbamate compositions are prepared by reacting an amine with carbon disulfide. The amine may be a primary or a secondary amine. The amines may be primary or secondary amines, with secondary
0 amines most preferred. The amines generally may contain hydrocarbyl groups. Each hydrocarbyl group may independently contain from one up to about 40, or from about two up to about 30, or from three up to about 24, or even up to about 12 carbon atoms. Examples of groups which may be on the amines include ethyl, propyl, butyl, hexyl, octyl and dodecyl groups.

In one embodiment, the amines are primary amines. Examples of primary amines
5 useful in the present invention include ethylamine, propylamine, butylamine, 2-ethylhexylamine, octylamine, and dodecylamine.

In one embodiment, the primary amine is a fatty (C₈₋₃₀) amine which include
0 n-octylamine, n-decylamine, n-dodecylamine, n-tetradecylamine, n-hexadecylamine, n-octadecylamine, oleyamine, etc. Also useful fatty amines include commercially available fatty amines such as "Armeen" amines (products available from Akzo Chemicals, Chicago, Illinois), such as Akzo's Armeen C, Armeen O, Armeen OL, Armeen T, Armeen HT, Armeen S and Armeen SD, wherein the letter designation relates to the fatty group, such as cocoa, oleyl, tallow, or stearyl groups.

Other useful primary amines include primary ether amines, such as those
5 represented by the formula, R"(OR')_xNH₂, wherein R' is a divalent alkylene group having from about 2 to about 6 carbon atoms; x is a number from one to about 150, or from one to about five, or one; and R" is a hydrocarbyl group of about 5 to about 150 carbon atoms. An example of an ether amine is available under the name SURFAM®
10 amines produced and marketed by Mars Chemical Company, Atlanta, Georgia. Preferred etheramines are exemplified by those identified as SURFAM P14B (decyloxypropylamine), SURFAM P16A (linear C₁₆), SURFAM P17B (tridecyloxypropylamine). The

carbon chain lengths (i.e., C₁₄, etc.) of the SURFAMS described above and used hereinafter are approximate and include the oxygen ether linkage.

In one embodiment, the amine is a tertiary-aliphatic primary amine. Generally, the aliphatic group, preferably an alkyl group, contains from about 4 to about 30, or from about 6 to about 24, or from about 8 to about 22 carbon atoms. Usually the tertiary alkyl primary amines are monoamines represented by the formula $R_1-C(R_1')_2-NH_2$, wherein R₁ is a hydrocarbyl group containing from one to about 27 carbon atoms and R₁' is a hydrocarbyl group containing from 1 to about 12 carbon atoms. Such amines are illustrated by tert-butylamine, tert-hexylamine, 1-methyl-1-amino-cyclohexane, tert-octylamine, tert-decylamine, tert-dodecylamine, tert-tetradecylamine, tert-hexadecylamine, tert-octadecylamine, tert-tetracosanylamine, and tert-octacosanylamine.

Mixtures of amines are also useful for the purposes of this invention. Illustrative of amine mixtures of this type are "Primene 81R" which is a mixture of C₁₁-C₁₄ tertiary alkyl primary amines and "Primene JMT" which is a similar mixture of C₁₈-C₂₂ tertiary alkyl primary amines (both are available from Rohm and Haas Company). The tertiary alkyl primary amines and methods for their preparation are known to those of ordinary skill in the art. The tertiary alkyl primary amine useful for the purposes of this invention and methods for their preparation are described in U.S. Patent 2,945,749 which is hereby incorporated by reference for its teaching in this regard.

In another embodiment, the amine is a secondary amine. Specific of secondary amines include dimethylamine, diethylamine, dipropylamine, dibutylamine, diamylamine, dihexylamine, diheptylamine, methylethylamine, ethylbutylamine, ethylamylamine and the like. In one embodiment, the secondary amines may be cyclic amines such as piperidine, piperazine, morpholine, etc.

In one embodiment, the dithiocarbamate compound (A) is prepared by reacting one or more dithiocarbamic acids or salts with an unsaturated amide. Examples of unsaturated amides include acrylamide, N,N'-methylene bis(acrylamide), methacrylamide, crotonamide, and the like. In one embodiment, the dithiocarbamate containing composition is derived from the reaction product of a diamylamine or dibutylamine with carbon disulfide which forms a dithiocarbamic acid or a salt which is ultimately reacted with a acrylamide. If the reaction products of the dithiocarbamic acid or salt and an

unsaturated amide has additional NH group which are capable of reacting, then the reaction product may be further reacted with a linking or a coupling compound, such as formaldehyde or paraformaldehyde. The reaction products of dithiocarbamic acids and salts with unsaturated amides are disclosed in U.S. Patents 4,758,362 (Butke) and 4,997,969 (Luciani) which are incorporated by reference for their disclosures of dithiocarbamic acids and salts, unsaturated amides and their reaction products including coupled products.

In one embodiment, as less the dithiocarbamate composition (A) is a reaction product of a dithiocarbamic acid or salt with an unsaturated acid, anhydride or ester. Examples of unsaturated carboxylic acids and anhydrides include acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, and maleic anhydride. If an unsaturated carboxylic acid or anhydride is used, an ester may then be formed by subsequent reaction of the dithiocarbamate-unsaturated carboxylic acid or anhydride adduct with an alcohol such as those alcohols discussed herein. In one embodiment, the alcohol has from 1 to about 12 carbon atoms.

In one embodiment, the unsaturated carboxylic acid, or anhydride or ester includes maleic, fumaric, acrylic, methacrylic, itaconic, citraconic acids and esters. The ester may be represented by one of the formulae: $(R_1)_2C=C(R_1)C(O)OR_2$, or $R_2O-(O)C-HC=CH-C(O)OR_2$, wherein each R_1 and R_2 are independently hydrogen or a hydrocarbyl group having 1 to about 18, or to about 12, or to about 8 carbon atoms, R_1 is hydrogen or an alkyl group having from 1 to about 6 carbon atoms. In one embodiment, R_1 is preferably hydrogen or a methyl group.

Examples of unsaturated carboxylic esters include methyl acrylate, ethyl acrylate, 2-ethylhexyl acrylate, 2-hydroxyethyl acrylate, ethyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, 2-hydroxypropyl acrylate, ethyl maleate, butyl maleate and 2-ethylhexyl maleate. The above list includes mono- as well as diesters of maleic, fumaric, and itaconic acids and anhydrides. In one embodiment, the dithiocarbamate acid or salt is formed from diethylamine or dibutylamine and carbon disulfide. The resulting dithiocarbamic acid is then reacted with methyl acrylate.

In another embodiment, the unsaturated carboxylic ester is a vinyl ester. The vinyl ester may be represented by the formula $R_1CH=CH-O(O)CR_2$, wherein R_1 is a hydrocarbyl group having from 1 to about 30, or to about 12 carbon atoms, preferably

hydrogen, and R_2 is a hydrocarbyl group having 1 to about 30, or to about 12, or to about 8 carbon atoms. Examples of vinyl esters include vinyl acetate, vinyl 2-ethylhexanoate, vinyl butanoate, etc.

In one embodiment, the dithiocarbamate compound (A) is a reaction product of a dithiocarbamic acid or salt and a vinyl ether. The vinyl ether is represented by the formula $R_1\text{-CH=CH-OR}_2$ wherein R_1 is independently hydrogen or a hydrocarbyl group having from 1 up to about 30, or up to about 24, or up to about 12 carbon atoms. R_2 is a hydrocarbyl group defined the same as R_1 . Examples of vinyl ethers include methyl vinyl ether, propyl vinyl ether, 2-ethylhexyl vinyl ether and the like.

In one embodiment, the dithiocarbamate compound (A) is an alkylene-coupled dithiocarbamate. The alkylene-coupled dithiocarbamates useful in the present invention may be prepared by the reaction of a salt of a dithiocarbamic acid, described above, with a suitable dihalogen containing hydrocarbon. The reaction is generally carried out at a temperature within the range from about 25°C up to about 150°C, or up to about 100°C. U.S. Patent 3,876,550 issued to Holubec describes alkylene dithiocarbamate compounds, and U.S. Patents 1,726,647 and 1,736,429, issued to Cadwell describe, phenylmethylen bis(dithiocarbamates) and methods of making the same. These patents are incorporated by reference for their teachings related to dithiocarbamate compounds and methods for preparing the same. In one embodiment, the alkylene-coupled dithiocarbamate is derived from di-n-butyl amine, carbon disulfide and methylene dichloride.

In another embodiment, the dithiocarbamate compound is a bis(S-alkyldithiocarbamoyl) disulfide. These materials have previously been referred to as sulfur-coupled dithiocarbamates. The disulfides are prepared by (A) reacting a sulfur halide with about a stoichiometric equivalent of (i) at least one olefinic hydrocarbon, or (ii) an aldehyde or ketone, at a temperature and for a period of time sufficient to produce a di(halohydrocarbyl)sulfur intermediate or a dialdehyde or diketone sulfur intermediate, and (B) reacting the intermediate with a salt of a dithiocarbamate in an amount sufficient generally to replace both halo groups with the dithiocarbamate groups or to react with both carbonyl groups of the dialdehyde or diketone. The sulfur halide utilized in the first step (A) may be sulfur monochloride (i.e., S_2Cl_2), sulfur dichloride, sulfur monobromide, sulfur dibromide, or mixtures of any of the above sulfur halides with elemental sulfur in varying amounts.

The sulfur halide utilized in the first step (A) may be sulfur monochloride (i.e., S_2Cl_2), sulfur dichloride, sulfur monobromide, sulfur dibromide, or mixtures of any of the above sulfur halides with elemental sulfur in varying amounts. Various olefins and olefin mixtures may be used as the starting material in step (A). The olefins are disclosed below for the organic polysulfide. Specific examples of aldehydes that may be reacted with sulfur halides include, for example, acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde, 2-ethyl-hexanal, and cyclohexanecarboxaldehyde. Examples of ketones include dimethyl ketone, methyl ethyl ketone, diethyl ketone, methyl isopropyl ketone, methyl isobutyl ketone, etc.

The reaction between the sulfur intermediate and the dithiocarbamate salts generally is conducted from ambient temperature to the reflux temperature of the mixture. The reaction is conducted until the reaction is completed which is generally from about 5 to about 24 hours. At the end of the reaction, the aqueous phase is separated, and the product is recovered from the organic phase.

The bis(S-alkyldithiocarbamoyl) disulfides also may be prepared by a process which comprises the steps of (A) reacting an olefinic hydrocarbon with a halogen to produce a halogen-containing intermediate, and (B) reacting said intermediate with an alkali metal sulfide and a salt of a dithiocarbamate in an amount sufficient to replace the halogen groups present partially with dithiocarbamate groups and/or partially with sulfide groups. The bis(S-alkyldithiocarbamoyl) disulfides are described in U.S. Patent 2,599,350, issued to Rudel et al. This patent is incorporated by reference for its disclosure of bis(S-alkyldithiocarbamoyl) disulfide.

Phosphorus or Boron Agents:

As described above, the molybdenum containing composition salts are used in combination with (i) an organic polysulfide or an ashless dithiocarbamate containing composition, and (ii) at least one phosphorus or boron containing antiwear/extreme pressure agent selected from the group consisting of a metal thiophosphate, a phosphoric acid ester or salt thereof, a phosphorus-containing carboxylic acid, ester, ether, or amide, a borated dispersant, an alkali metal borate, a borated fatty amine, a borated phospholipid, and a borate ester. The phosphorus or boron containing agents are typically present in the lubricants and functional fluids at a level of up to about 20% by weight, preferably up to about 10% by weight, based on the total weight of the lubricant,

functional fluid, or grease. Typically, the phosphorus or boron containing antiwear/extreme pressure agent is present at a level from about 0.1%, or from about 0.5%, or from about 0.8% by weight. The phosphorus or boron containing antiwear/extreme pressure agent is present in an amount up to about 10%, or up to about 3%, or up to about 2% by weight. In one embodiment, the lubricating compositions, functional fluids, and greases contain more than 0.01% phosphorus, preferably greater than 0.05% phosphorus.

Examples of phosphorus or boron containing antiwear/extreme pressure agents include a metal thiophosphate; a phosphoric acid ester or salt thereof; a phosphorus-containing carboxylic acid, ester, ether, or amide; a borated dispersant; an alkali metal borate; a borated fatty amine; a borated phospholipid; and a borate ester. The phosphorus acids include the phosphoric, phosphonic, phosphinic and thiophosphoric acids including dithiophosphoric acid as well as the monothiophosphoric acid, thiophosphinic and thiophosphonic acids.

In one embodiment, phosphorus or boron containing antiwear/extreme pressure agent is a phosphorus acid ester prepared by reacting one or more phosphorus acid or anhydride with an alcohol containing from one, or about 3 carbon atoms. The alcohol generally contains up to about 30, or up to about 24, or up to about 12 carbon atoms. The phosphorus acid or anhydride is generally an inorganic phosphorus reagent, such as phosphorus pentoxide, phosphorus trioxide, phosphorus tetroxide, phosphorus acid, phosphorus halide, lower phosphorus esters, or a phosphorus sulfide, including phosphorus pentasulfide, and the like. Preferred phosphorus acids or anhydrides are phosphorus pentoxide, phosphorus pentasulfide and phosphorus trichloride. Lower phosphorus acid esters generally contain from 1 to about 7 carbon atoms in each ester group. The phosphorus acid ester may be a mono-, di- or triphosphoric acid ester. Alcohols used to prepare the phosphorus acid esters include butyl, amyl, 2-ethylhexyl, hexyl, octyl, oleyl, and cresol alcohols. Examples of commercially available alcohols include Alfol 810 (a mixture of primarily straight chain, primary alcohols having from 8 to 10 carbon atoms); Alfol 1218 (a mixture of synthetic, primary, straight-chain alcohols containing 12 to 18 carbon atoms); Alfol 20+ alcohols (mixtures of C₁₈-C₂₈ primary alcohols having mostly C₂₀ alcohols as determined by GLC (gas-liquid-chromato-

graphy)); and Alfol 22+ alcohols (C_{18} - C_{28} primary alcohols containing primarily C_{22} alcohols). Alfol alcohols are available from Continental Oil Company.

Another example of a commercially available alcohol mixtures are Adol 60 (about 75% by weight of a straight chain C_{22} primary alcohol, about 15% of a C_{20} primary alcohol and about 8% of C_{18} and C_{24} alcohols) and Adol 320 (oleyl alcohol). The Adol alcohols are marketed by Ashland Chemical.

A variety of mixtures of monohydric fatty alcohols derived from naturally occurring triglycerides and ranging in chain length of from about C_8 to C_{18} are available from Procter & Gamble Company. These mixtures contain various amounts of fatty alcohols containing mainly 12, 14, 16, or 18 carbon atoms. For example, CO-1214 is a fatty alcohol mixture containing 0.5% of C_{10} alcohol, 66.0% of C_{12} alcohol, 26.0% of C_{14} alcohol and 6.5% of C_{16} alcohol.

Another group of commercially available mixtures include the "Neodol" products available from Shell Chemical Co. For example, Neodol 23 is a mixture of C_{12} and C_{13} alcohols; Neodol 25 is a mixture of C_{12} and C_{15} alcohols; and Neodol 45 is a mixture of C_{14} to C_{15} linear alcohols. Neodol 91 is a mixture of C_9 , C_{10} and C_{11} alcohols.

Fatty vicinal diols also are useful and these include those available from Ashland Oil under the general trade designation Adol 114 and Adol 158. The former is derived from a straight chain alpha olefin fraction of C_{11} - C_{14} , and the latter is derived from a C_{15} - C_{18} fraction.

Examples of useful phosphorus acid esters include the phosphoric acid esters prepared by reacting a phosphoric acid or anhydride with cresol alcohols. An example of these phosphorus acid esters is tricresylphosphate.

In another embodiment, the phosphorus or boron antiwear/extreme pressure agent is a thiophosphorus acid ester or salt thereof. The thiophosphorus acid ester may be prepared by reacting a phosphorus sulfide, such as those described above, with an alcohol, such as those described above. The thiophosphorus acid esters may be mono- or dithiophosphorus acid esters. Thiophosphorus acid esters are also referred to generally as thiophosphoric acids.

In one embodiment, the phosphorus acid ester is a monothiophosphoric acid ester or a monothiophosphate. Monothiophosphates may be prepared by the reaction of a sulfur source with a dihydrocarbyl phosphite. The sulfur source may for instance be

elemental sulfur. The sulfur source may also be a monosulfide, such as a sulfur coupled olefin or a sulfur coupled dithiophosphate. Elemental sulfur is a preferred sulfur source. The preparation of monothiophosphates is disclosed in U.S. Patent 4,755,311 and PCT Publication WO 87/07638, which are incorporated herein by reference for their disclosure of monothiophosphates, sulfur sources, and the process for making monothiophosphates. Monothiophosphates may also be formed in the lubricant blend by adding a dihydrocarbyl phosphite to a lubricating composition containing a sulfur source, such as a sulfurized olefin. The phosphite may react with the sulfur source under blending conditions (i.e., temperatures from about 30°C to about 100°C or higher) to form the monothiophosphate.

In another embodiment, the phosphorus or boron antiwear/extreme pressure agent is a dithiophosphoric acid or phosphorodithioic acid. The dithiophosphoric acid may be represented by the formula $(RO)_2PSSH$ wherein each R is independently a hydrocarbyl group containing from about 3 to about 30 carbon atoms. R generally contains up to about 18, or to about 12, or to about 8 carbon atoms. Examples R include isopropyl, isobutyl, n-butyl, sec-butyl, the various amyl, n-hexyl, methylisobutyl carbinyl, heptyl, 2-ethylhexyl, isooctyl, nonyl, behenyl, decyl, dodecyl, and tridecyl groups. Illustrative lower alkylphenyl R groups include butylphenyl, amylphenyl, heptylphenyl, etc. Examples of mixtures of R groups include: 1-butyl and 1-octyl; 1-pentyl and 2-ethyl-1-hexyl; isobutyl and n-hexyl; isobutyl and isoamyl; 2-propyl and 2-methyl-4-pentyl; isopropyl and sec-butyl; and isopropyl and isooctyl.

In one embodiment, the dithiophosphoric acid may be reacted with an epoxide or a glycol. This reaction product may be used alone, or further reacted with a phosphorus acid, anhydride, or lower ester. The epoxide is generally an aliphatic epoxide or a styrene oxide. Examples of useful epoxides include ethylene oxide, propylene oxide, butene oxide, octene oxide, dodecene oxide, styrene oxide, etc. Propylene oxide is preferred. The glycols may be aliphatic glycols having from 1 to about 12, preferably about 2 to about 6, more preferably 2 or 3 carbon atoms, or aromatic glycols. Glycols include ethylene glycol, propylene glycol, catechol, resorcinol, and the like. The dithiophosphoric acids, glycols, epoxides, inorganic phosphorus reagents and methods of reacting the same are described in U.S. patent 3,197,405 and U.S. patent 3,544,465 which are incorporated herein by reference for their disclosure to these.

The following Examples P-1 and P-2 exemplify the preparation of useful phosphorus acid esters.

Example P-1

Phosphorus pentoxide (64 grams) is added at 58°C over a period of 45 minutes to 514 grams of hydroxypropyl O,O-di(4-methyl-2-pentyl)phosphorodithioate (prepared by reacting di(4-methyl-2-pentyl)-phosphorodithioic acid with 1.3 moles of propylene oxide at 25°C). The mixture is heated at 75°C for 2.5 hours, mixed with a diatomaceous earth and filtered at 70°C. The filtrate contains 11.8% by weight phosphorus, 15.2% by weight sulfur, and an acid number of 87 (bromophenol blue).

Example P-2

A mixture of 667 grams of phosphorus pentoxide and the reaction product of 3514 grams of diisopropyl phosphorodithioic acid with 986 grams of propylene oxide at 50°C is heated at 85°C for 3 hours and filtered. The filtrate contains 15.3% by weight phosphorus, 19.6% by weight sulfur, and an acid number of 126 (bromophenol blue).

Acidic phosphoric acid esters may be reacted with an amine compound or a metallic base to form an amine or metal salt. The salts may be formed separately and then the salt of the phosphorus acid ester may be added to the lubricating composition. Alternately, the salts may also be formed *in situ* when the acidic phosphorus acid ester is blended with other components to form a fully formulated lubricating composition.

The amine salts of the phosphorus acid esters may be formed from ammonia, or an amine, including monoamines and polyamines. The amines may be primary amines, secondary amines or tertiary amines. In one embodiment, the amines are one or more of the amines described above for preparing the dithiocarbamates. Useful amines include those amines disclosed in U.S. Patent 4,234,435 at Col. 21, line 4 to Col. 27, line 50, these passages being incorporated herein by reference.

The monoamines generally contain from 1 up to about 24 carbon atoms, or up to about 12, or up to about 6 carbon atoms. Examples of monoamines include methylamine, ethylamine, propylamine, butylamine, octylamine, and dodecylamine, dimethylamine, diethylamine, dipropylamine, dibutylamine, methyl butylamine, ethyl hexylamine, trimethylamine, tributylamine, methyl diethylamine, ethyl dibutylamine, etc.

In one embodiment, the amine may be a fatty (C₄₋₃₀) amine which include n-hexylamine, n-octylamine, n-decylamine, n-dodecylamine, n-tetradecylamine,

n-hexadecylamine, n-octadecylamine, oleylamine, etc. Also useful fatty amines include commercially available fatty amines such as "Armeen" amines (products available from Armak Chemicals, Chicago, Illinois), such as Armak's Armeen-C, Armeen-O, Armeen-OL, Armeen-T, Armeen-HT, Armeen S and Armeen SD, wherein the letter designation relates to the fatty group, such as cocoa, oleyl, tallow, or soya groups.

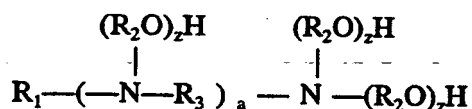
Other useful amines include primary ether amines, such as those represented by the formula, $R''(OR')_xNH_2$, wherein R' is a divalent alkylene group having about 2 to about 6 carbon atoms, x is a number from one to about 150 (preferably one), and R'' is a hydrocarbyl group of about 5 to about 150 carbon atoms. An example of an ether amine is available under the name SURFAM® amines produced and marketed by Mars Chemical Company, Atlanta, Georgia. Preferred etheramines are exemplified by those identified as SURFAM P14B (decyloxypropylamine), SURFAM P16A (linear C_{16}), SURFAM P17B (tridecyloxypropylamine). The carbon chain lengths (i.e., C_{14} , etc.) of the SURFAMS described above and used hereinafter are approximate and include the oxygen ether linkage.

In one embodiment, the amine may be a hydroxyamine. Typically, the hydroxyamines are primary, secondary or tertiary alkanol amines or mixtures thereof. Such amines can be represented by the formulae: $H_2-N-R'-OH$, $H(R'_1)_N-R'-OH$, and $(R'_1)_2-N-R'-OH$, wherein each R'_1 is independently a hydrocarbyl group having from one to about eight carbon atoms or hydroxyhydrocarbyl group having from one to about eight carbon atoms, or from one to about four, and R' is a divalent hydrocarbyl group of about two to about 18 carbon atoms, or from two to about four. The group $-R'-OH$ in such formulae represents the hydroxyhydrocarbyl group. R' can be an acyclic, alicyclic or aromatic group. Typically, R' is an acyclic straight or branched alkylene group such as an ethylene, propylene, 1,2-butylene, 1,2-octadecylene, etc. group. Where two R'_1 groups are present in the same molecule they can be joined by a direct carbon-to-carbon bond or through a heteroatom (e.g., oxygen, nitrogen or sulfur) to form a 5-, 6-, 7- or 8-membered ring structure. Examples of such heterocyclic amines include N-(hydroxyl lower alkyl)-morpholines, -thiomorpholines, -piperidines, -oxazolidines, -thiazolidines and the like. Typically, however, each R'_1 is independently a methyl, ethyl, propyl, butyl, pentyl or hexyl group.

Examples of these alkanolamines include mono-, di-, and triethanolamine, diethylethanolamine, ethylethanolamine, butyldiethanolamine, etc.

The hydroxyamines may also be an ether N-(hydroxyhydrocarbyl)amine. These are hydroxypoly(hydrocarbyloxy) analogs of the above-described hydroxyamines (these analogs also include hydroxyl-substituted oxyalkylene analogs). Such N-(hydroxyhydrocarbyl) amines can be conveniently prepared by reaction of one or more of the above epoxides with aforescribed amines and may be represented by the formulae: $H_2N-(R'O)_x-H$, $H(R'_1)-N-(R'O)_x-H$, and $(R'_1)_2-N-(R'O)_x-H$, wherein x is a number from about 2 to about 15 and R_1 and R' are as described above. R'_1 may also be a hydroxypoly(hydrocarbyloxy) group.

The amines may be hydroxyamines, such as those represented by the formula



wherein R_1 is a hydrocarbyl group generally containing from about 6 to about 30 carbon atoms; R_2 and each R_3 is independently an alkylene group containing up to about 5 carbon atoms, preferably an ethylene or propylene group; a is zero or one; and each z is independently a number from zero to about 10, with the proviso that at least one z is at least one. These hydroxyamines can be prepared by techniques well known in the art and many such hydroxyamines are commercially available. The hydroxy amines include mixtures of amines such as obtained by the hydrolysis of fatty oils (e.g., tallow oils, sperm oils, coconut oils, etc.). Specific examples of fatty amines, containing from about 6 to about 30 carbon atoms, include saturated as well as unsaturated aliphatic amines, such as octyl amine, decyl amine, lauryl amine, stearyl amine, oleyl amine, dodecyl amine, and octadecyl amine.

Useful hydroxyamines wherein a in the above formula is zero include 2-hydroxyethyl, hexylamine; 2-hydroxyethyloctylamine; 2-hydroxyethyl, pentadecylamine; 2-hydroxyethyl, oleylamine; 2-hydroxyethyl, soyamine; bis(2-hydroxyethyl) hexylamine;

bis(2-hydroxyethyl)oleylamine; and mixtures thereof. Also included are the comparable members wherein in the above formula at least one of z is at least 2, as for example, 2-hydroxyethoxyethyl, hexylamine.

A number of hydroxyamines wherein a in the above formula is zero are available from the Armak Chemical Division of Akzona, Inc., Chicago, Illinois, under the general trade designations "Ethomeen" and "Propomeen". Specific examples of such products include: Ethomeen C/15 which is an ethylene oxide condensate of a coco alkyl amine containing about 5 moles of ethylene oxide; Ethomeen C/20 and C/25 which are ethylene oxide condensation products from coco alkyl amine containing about 10 and 15 moles of ethylene oxide, respectively; Ethomeen O/12 which is an ethylene oxide condensation product of oleylamine containing about 2 moles of ethylene oxide per mole of amine; Ethomeen S/15 and S/20 which are ethylene oxide condensation products with stearyl amine containing about 5 and 10 moles of ethylene oxide per mole of amine, respectively; Ethomeen T/12, T/15 and T/25 which are ethylene oxide condensation products of tallow amine containing about 2, 5 and 15 moles of ethylene oxide per mole of amine, respectively; and Propomeen O/12 which is the condensation product of one mole of oleylamine with 2 moles propylene oxide.

Commercially available examples of alkoxyated amines where a in the above formula is one include Ethoduomeen T/13 and T/20 which are ethylene oxide condensation products of N-tallow trimethylenediamine containing 3 and 10 moles of ethylene oxide per mole of diamine, respectively.

The amine may also be a polyamine. The polyamines include alkoxyated diamines, fatty diamines, alkylenepolyamines, hydroxy containing polyamines, condensed polyamines and heterocyclic polyamines. Commercially available examples of alkoxyated diamines include those amines where a in the above formula is one. Examples of these amines include Ethoduomeen T/13 and T/20 which are ethylene oxide condensation products of N-tallowtrimethylenediamine containing 3 and 10 moles of ethylene oxide per mole of diamine, respectively.

In another embodiment, the polyamine is a fatty diamine. The fatty diamines include mono- or dialkyl, symmetrical or asymmetrical ethylenediamines, propanediamines (1,2, or 1,3), and polyamine analogs of the above. Suitable commercial fatty polyamines are Duomeen C (N-coco-1,3-diaminopropane), Duomeen S

(N-soya-1,3-diaminopropane), Duomeen T (N-tallow-1,3-diaminopropane), and Duomeen O (N-oleyl-1,3-diaminopropane). "Duomeens" are commercially available from Armac Chemical Co., Chicago, Illinois.

In another embodiment, the amine is an alkylenepolyamine. Alkylenepolyamines are represented by the formula $HR_1N-(\text{Alkylene-N})_n-(R_1)_2$, wherein each R_1 is independently hydrogen; or an aliphatic or hydroxy-substituted aliphatic group of up to about 30 carbon atoms; \bar{M}_n is a number from 1 to about 10, or from about 2 to about 7, or from about 2 to about 5; and the "Alkylene" group has from 1 to about 10 carbon atoms, or from about 2 to about 6, or from about 2 to about 4. In another embodiment, R_1 is defined the same as R'_1 above. Such alkylenepolyamines include methylenepolyamines, ethylenepolyamines, butylenepolyamines, propylenepolyamines, pentylenepolyamines, etc. The higher homologs and related heterocyclic amines, such as piperazines and N-amino alkyl-substituted piperazines, are also included. Specific examples of such polyamines are ethylenediamine, triethylenetetramine, tris-(2-aminoethyl)amine, propylenediamine, trimethylenediamine, tripropylenetetramine, triethylenetetraamine, tetraethylenepentamine, hexaethyleneheptamine, pentaethylenehexamine, etc. Higher homologs obtained by condensing two or more of the above-noted alkyleneamines are similarly useful as are mixtures of two or more of the aforescribed polyamines.

In one embodiment, the polyamine is an ethylenepolyamine. Such polyamines are described in detail under the heading Ethylene Amines in Kirk Othmer's "Encyclopedia of Chemical Technology", 2d Edition, Vol. 7, pages 22-37, Interscience Publishers, New York (1965). Ethylenepolyamines are often a complex mixture of polyalkylenepolyamines including cyclic condensation products. Other useful types of polyamine mixtures are those resulting from stripping of the above-described polyamine mixtures to leave, as residue, what is often termed "polyamine bottoms". In general, alkylenepolyamine bottoms can be characterized as having less than 2%, usually less than 1% (by weight) material boiling below about 200°C. A typical sample of such ethylenepolyamine bottoms obtained from the Dow Chemical Company of Freeport, Texas designated "E-100" has a specific gravity at 15.6°C of 1.0168, a percent nitrogen by weight of 33.15 and a viscosity at 40°C of 121 centistokes. Gas chromatography analysis of such a sample contains about 0.93% "Light Ends" (most probably diethylenetriamine), 0.72%

tirethylenetetraamine, 21.74% tetraethylenepentaamine and 76.61% pentaethylenehexamine and higher analogs. These alkylenepolyamine bottoms include cyclic condensation products, such as piperazine, and higher analogs of diethylenetriamine, triethylenetetramine and the like. These alkylenepolyamine bottoms may be reacted solely with the acylating agent or they may be used with other amines, polyamines, or mixtures thereof.

Another useful polyamine is a condensation reaction between at least one hydroxy compound with at least one polyamine reactant containing at least one primary or secondary amino group. The hydroxy compounds are preferably polyhydric alcohols or polyhydric amines. The polyhydric alcohols are described below. In one embodiment, the hydroxy compounds are polyhydric amines. Polyhydric amines include any of the above-described monoamines reacted with an alkylene oxide (e.g., ethylene oxide, propylene oxide, butylene oxide, etc.) having from two to about 20, or from two to about four carbon atoms. Examples of polyhydric amines include tri-(hydroxypropyl)amine, tris-(hydroxymethyl)amino methane, 2-amino-2-methyl-1,3-propanediol, N,N,N',N'-tetrakis (2-hydroxypropyl) ethylenediamine, and N,N,N',N'-tetrakis (2-hydroxyethyl) ethylenediamine, preferably tris(hydroxymethyl) aminomethane (THAM).

Polyamines which may react with the polyhydric alcohol or amine to form the condensation products or condensed amines, are described above. Preferred polyamines include triethylenetetramine (TETA), tetraethylenepentamine (TEPA), pentaethylenehexamine (PEHA), and mixtures of polyamines such as the above-described "amine bottoms". The condensation reaction of the polyamine reactant with the hydroxy compound is conducted at an elevated temperature, usually from about 60°C to about 265°C, or from about 220°C to about 250°C in the presence of an acid catalyst.

The amine condensates and methods of making the same are described in PCT publication WO 86/05501 and U.S. Patent 5,230,714 (Steckel) which are incorporated by reference for its disclosure to the condensates and methods of making. A particularly useful amine condensate is prepared from HPA Taft Amines (amine bottoms available commercially from Union Carbide Co. with typically 34.1% by weight nitrogen and a nitrogen distribution of 12.3% by weight primary amine, 14.4% by weight secondary amine and 7.4% by weight tertiary amine), and tris(hydroxymethyl)aminomethane (THAM).

In another embodiment, the polyamines are polyoxyalkylene polyamines, e.g. polyoxyalkylene diamines and polyoxyalkylene triamines, having average molecular weights ranging from about 200 to about 4000, or from about 400 to about 2000. The preferred polyoxyalkylene polyamines include the polyoxyethylene and polyoxypropylene diamines and the polyoxypropylene triamines. The polyoxyalkylene polyamines are commercially available and may be obtained, for example, from the Jefferson Chemical Company, Inc. under the trade name "Jeffamines D-230, D-400, D-1000, D-2000, T-403, etc.". U.S. Patents 3,804,763 and 3,948,800 are expressly incorporated herein by reference for their disclosure of such polyoxyalkylene polyamines and acylated products made therefrom.

In another embodiment, the polyamines are hydroxy-containing polyamines. Hydroxy-containing polyamine analogs of hydroxy monoamines, particularly alkoxylated alkylene polyamines, e.g., N,N(diethanol)ethylene diamines can also be used. Such polyamines can be made by reacting the above-described alkylene amines with one or more of the above-described alkylene oxides. Similar alkylene oxide-alkanol amine reaction products may also be used such as the products made by reacting the above described primary, secondary or tertiary alkanol amines with ethylene, propylene or higher epoxides in a 1.1 to 1.2 molar ratio. Reactant ratios and temperatures for carrying out such reactions are known to those skilled in the art. Specific examples of hydroxy-containing polyamines include N-(2-hydroxyethyl) ethylenediamine, N,N'-bis(2-hydroxyethyl)-ethylenediamine, 1-(2-hydroxyethyl)piperazine, mono(hydroxypropyl)-substituted tetraethylenepentamine, N-(3-hydroxybutyl)-tetramethylene diamine, etc. Higher homologs obtained by condensation of the above illustrated hydroxy-containing polyamines through amino groups or through hydroxy groups are likewise useful. Condensation through amino groups results in a higher amine accompanied by removal of ammonia while condensation through the hydroxy groups results in products containing ether linkages accompanied by removal of water. Mixtures of two or more of any of the above described polyamines are also useful.

In another embodiment, the amine is a heterocyclic amine. The heterocyclic polyamines include aziridines, azetidines, azolidines, tetra- and dihydropyridines, pyrroles, indoles, piperidines, imidazoles, di- and tetrahydroimidazoles, piperazines, iso-indoles, purines, morpholines, thiomorpholines, N-aminoalkylmorpholines, N-amino-

alkylthiomorpholines, N-aminoalkylpiperazines, N,N'-diaminoalkylpiperazines, azepines, azocines, azonines, azecines and tetra-, di- and perhydro derivatives of each of the above and mixtures of two or more of these heterocyclic amines. Preferred heterocyclic amines are the saturated 5- and 6-membered heterocyclic amines containing only nitrogen, oxygen and/or sulfur in the hetero ring, especially the piperidines, piperazines, thiomorpholines, morpholines, pyrrolidines, and the like. Piperidine, aminoalkyl substituted piperidines, piperazine, aminoalkyl substituted piperazines, morpholine, aminoalkyl substituted morpholines, pyrrolidine, and aminoalkyl-substituted pyrrolidines, are especially preferred. Usually the aminoalkyl substituents are substituted on a nitrogen atom forming part of the hetero ring. Specific examples of such heterocyclic amines include N-aminopropylmorpholine, N-aminoethylpiperazine, and N,N'-diaminoethylpiperazine. Hydroxy heterocyclic amines are also useful. Examples include N-(2-hydroxyethyl)cyclohexylamine, 3-hydroxycyclopentylamine, parahydroxyaniline, N-hydroxyethylpiperazine, and the like.

The metal salts of the phosphorus acid esters are prepared by the reaction of a metal base with the phosphorus acid ester. The metal base may be any metal compound capable of forming a metal salt. Examples of metal bases include metal oxides, hydroxides, carbonates, sulfates, borates, or the like. The metals of the metal base include Group IA, IIA, IB through VIIB, and VIII metals (CAS version of the Periodic Table of the Elements). These metals include the alkali metals, alkaline earth metals and transition metals. In one embodiment, the metal is a Group IIA metal, such as calcium or magnesium, Group IIB metal, such as zinc, or a Group VIIB metal, such as manganese. Preferably the metal is magnesium, calcium, manganese or zinc. Examples of metal compounds which may be reacted with the phosphorus acid include zinc hydroxide, zinc oxide, copper hydroxide, copper oxide, etc.

In one embodiment, phosphorus or boron containing antiwear/extreme pressure agent is a metal thiophosphate, preferably a metal dithiophosphate. The metal thiophosphate is prepared by means known to those in the art. Examples of metal dithiophosphates include zinc isopropyl, methylamyl dithiophosphate, zinc isopropyl isooctyl dithiophosphate, barium di(nonyl) dithiophosphate, zinc di(cyclohexyl) dithiophosphate, zinc di(isobutyl) dithiophosphate, calcium di(hexyl) dithiophosphate, zinc isobutyl isoamyl dithiophosphate, and zinc isopropyl secondary-butyl dithiophosphate.

The following Examples P-3 to P-6 exemplify the preparation of useful phosphorus acid ester salts.

Example P-3

5 A reaction vessel is charged with 217 grams of the filtrate from Example P-1. A commercial aliphatic primary amine (66 grams), having an average molecular weight of 191 in which the aliphatic radical is a mixture of tertiary alkyl radicals containing from 11 to 14 carbon atom, is added over a period of 20 minutes at 25-60°C. The resulting product has a phosphorus content of 10.2% by weight, a nitrogen content of 1.5% by weight, and an acid number of 26.3.

10 Example P-4

Following the procedures of Examples P-1 and P-3, 1320 parts of the product described in P-1 was reacted with 584 parts of the amine of P-3. The final product has 8.4% phosphorus and 10% sulfur.

Example P-5

15 The filtrate of Example P-2 (1752 grams) is mixed at 25-82°C with 764 grams of the aliphatic primary amine used in of Example P-3. The resulting product has 9.9% phosphorus, 2.7% nitrogen, and 12.6% sulfur.

Example P-6

20 Phosphorus pentoxide (852 grams) is added to 2340 grams of iso-octyl alcohol over a period of 3 hours. The temperature increases from room temperature but is maintained below 65°C. After the addition is complete the reaction mixture is heated to 90°C and the temperature is maintained for 3 hours. Diatomaceous earth is added to the mixture, and the mixture is filtered. The filtrate has 12.4% phosphorus, a 192 acid neutralization number (bromophenol blue) and a 290 acid neutralization number (phenolphthalein).

25 The above filtrate is mixed with 200 grams of toluene, 130 grams of mineral oil, 1 gram of acetic acid, 10 grams of water and 45 grams of zinc oxide. The mixture is heated to 60-70°C under a pressure of 30 mm Hg. The resulting product mixture is filtered using a diatomaceous earth. The filtrate has 8.6% zinc and 7.0% phosphorus.

30 Example P-7

Alfol 8-10 (2628 parts, 18 moles) is heated to a temperature of about 45°C whereupon 852 parts (6 moles) of phosphorus pentoxide are added over a period of 45

minutes while maintaining the reaction temperature between about 45-65°C. The mixture is stirred an additional 0.5 hour at this temperature, and is thereafter heated at 70°C for about 2-3 hours. Primene 81-R (2362 parts, 12.6 moles) is added dropwise to the reaction mixture while maintaining the temperature between about 30-50°C. When all of the amine has been added, the reaction mixture is filtered through a filter aid, and the filtrate is the desired amine salt containing 7.4% phosphorus (theory, 7.1%).

Example P-8

Phosphorus pentoxide (208 grams) is added to the product prepared by reacting 280 grams of propylene oxide with 1184 grams of O,O'-di-isobutylphosphorodithioic acid at 30-60°C. The addition is made at a temperature of 50-60°C and the resulting mixture is then heated to 80°C and held at that temperature for 2 hours. The commercial aliphatic primary amine identified in Example P-3 (384 grams) is added to the mixture, while the temperature is maintained in the range of 30-60°C. The reaction mixture is filtered through diatomaceous earth. The filtrate has 9.3% phosphorus, 11.4% sulfur, 2.5% nitrogen, and a base number of 6.9 (bromophenol blue indicator).

In another embodiment, the phosphorus or boron antiwear/extreme pressure agent is a metal salt of (a) at least one dithiophosphoric acid and (b) at least one aliphatic or alicyclic carboxylic acid. The dithiophosphoric acids are described above. The carboxylic acid may be a monocarboxylic or polycarboxylic acid, usually containing from 1 to about 3, or just one carboxylic acid group. The preferred carboxylic acids are those having the formula RCOOH, wherein R is an aliphatic or alicyclic hydrocarbyl group preferably free from acetylenic unsaturation. R generally contains from about 2, or from about 4 carbon atoms. R generally contains up to about 40, or up to about 24, or to up to about 12 carbon atoms. In one embodiment, R contains from 4, or from about 6 up to about 12, or up to about 8 carbon atoms. In one embodiment, R is an alkyl group. Suitable acids include the butanoic, pentanoic, hexanoic, octanoic, nonanoic, decanoic, dodecanoic, octadecanoic and eicosanoic acids, as well as olefinic acids such as oleic, linoleic, and linolenic acids and linoleic acid dimer. A preferred carboxylic acid is 2-ethylhexanoic acid.

The metal salts may be prepared by merely blending a metal salt of a dithiophosphoric acid with a metal salt of a carboxylic acid in the desired ratio. The ratio of equivalents of dithiophosphoric acid to carboxylic acid is from about 0.5 up to about

400 to 1. The ratio may be from 0.5 up to about 200, or up to about 100, or up to about 50, or up to about 20 to 1. In one embodiment, the ratio is from 0.5 up to about 4.5 to one, preferably from about 2.5 up to about 4.25 to one. For this purpose, the equivalent weight of a dithiophosphoric acid is its molecular weight divided by the number of -PSSH groups therein, and the equivalent weight of a carboxylic acid is its molecular weight divided by the number of carboxy groups therein.

A second and preferred method for preparing the metal salts useful in this invention is to prepare a mixture of the acids in the desired ratio, such as those described above for the metal salts of the individual metal salts, and to react the acid mixture with one of the above described metal compounds. When this method of preparation is used, it is frequently possible to prepare a salt containing an excess of metal with respect to the number of equivalents of acid present; thus the metal salts may contain as many as 2 equivalents and especially up to about 1.5 equivalents of metal per equivalent of acid may be prepared. The equivalent of a metal for this purpose is its atomic weight divided by its valence. The temperature at which the metal salts are prepared is generally between about 30°C and about 150°C, preferably up to about 125°C. U.S. Patents 4,308,154 and 4,417,990 describe procedures for preparing these metal salts and disclose a number of examples of such metal salts. These patents are hereby incorporated by reference for those disclosures.

In one embodiment, the phosphorus or boron containing antiwear/extreme pressure agent is a phosphorus containing amide. The phosphorus containing amides are prepared by the reaction of one of the above describe phosphorus acids, preferably a dithiophosphoric acid, with an one of the above described unsaturated amides. The reaction product of the phosphorus acid and the unsaturated amide may be further reacted with a linking or a coupling compound, such as formaldehyde or paraformaldehyde. The phosphorus containing amides are known in the art and are disclosed in U.S. Patents 4,670,169, 4,770,807, and 4,876,374 which are incorporated by reference for their disclosures of phosphorus amides and their preparation.

In one embodiment, the phosphorus or boron antiwear/extreme pressure agent is a phosphorus containing carboxylic ester. The phosphorus containing carboxylic esters are prepared by reaction of one of the above-described phosphorus acids, preferably a dithiophosphoric acid, and one of the above described unsaturated carboxylic acids or

esters. If the carboxylic acid is used, the ester may then be formed by subsequent reaction of the phosphoric acid-unsaturated carboxylic acid adduct with an alcohol, such as those described herein.

In one embodiment, the phosphorus or boron containing antiwear/extreme pressure agent is a reaction product of a phosphorus acid, preferably a dithiophosphoric acid, and one of the above described vinyl ethers.

In another embodiment, the phosphorus or boron containing antiwear/extreme pressure agent is an alkali metal borate. Alkali metal borates are generally a hydrated particulate alkali metal borate which are known in the art. Alkali metal borates include mixed alkali and alkaline earth metal borates. These alkali metal borates are available commercially. Representative patents disclosing suitable alkali metal borates and their methods of manufacture include U.S. 3,997,454; 3,819,521; 3,853,772; 3,907,601; 3,997,454; and 4,089,790. These patents are incorporated by reference for their disclosures of alkali metal borates and methods of their manufacture.

In another embodiment, the phosphorus or boron containing antiwear/extreme pressure agent is a borated overbased compound, provided that the borated overbased compound is different than B(i) above. The borated overbased compounds are described above.

In another embodiment, the phosphorus or boron antiwear/extreme pressure agent is a borated fatty amine. The borated amines are prepared by reacting one or more of the above boron compounds, such as boric acid, with one or more of the above fatty amines, e.g. an amine having from about four to about eighteen carbon atoms. The borated fatty amines are prepared by reacting the amine with the boron compound at about 50°C to about 300°C, preferably about 100°C to about 250°C, and at a ratio of 3:1 to 1:3 equivalents of amine to equivalents of boron compound.

In another embodiment, the phosphorus or boron containing antiwear/extreme pressure agent is a borated epoxide. The borated fatty epoxides are generally the reaction product of one or more of the above boron compounds, with at least one epoxide. The epoxide is generally an aliphatic epoxide having at least 8, preferably about 10, more preferably about 12, up to about 24, preferably 20 carbon atoms. Examples of useful aliphatic epoxides include heptyl oxide, octyl oxide, stearyl oxide, oleyl oxide and the like. Mixtures of epoxides may also be used, for instance commercial mixtures of

epoxides having from 14 to about 16 carbon atoms and from 14 to about 18 carbon atoms. The borated fatty epoxides are generally known and are disclosed in U.S. Patent 4,584,115. This patent is incorporated by reference for its disclosure of borated fatty epoxides and methods for preparing the same.

5 In another embodiment, the phosphorus or boron containing antiwear/extreme pressure agent is a borated phospholipid. The borated phospholipids are prepared by reacting a combination of a phospholipid and a boron compound. Optionally, the combination may include an amine, an acylated nitrogen compound, such as reaction products of carboxylic acylating agents and polyamines, a carboxylic ester, such as
0 reaction products of carboxylic acylating agents and alcohols and optionally amines, a Mannich reaction product, or a basic or neutral metal salt of an organic acid compound. Phospholipids, sometimes referred to as phosphatides and phospholipins, may be natural or synthetic. Naturally derived phospholipids include those derived from fish, fish oil, shellfish, bovine brain, chicken eggs, sunflowers, soybean, corn, and cottonseed. Phospholipids may be derived from microorganisms, including blue-green algae, green algae,
5 and bacteria.

The reaction of the phospholipid, the boron compound, and the optional components usually occurs at a temperature from about 60°C to about 200°C, or from about 90°C up to about 150°C. The reaction is typically accomplished in about 0.5, or
0 about 2 up to about 10 hours. The boron compound and phospholipid are reacted at an atomic proportion ratio of boron to phosphorus from about one up to about six to one, preferably from about two up to about four to one, more preferably about three to one. When the combination includes additional components, the boron compound is reacted with the mixture of the phospholipid and one or more optional ingredients in an amount
5 of one atomic proportion of boron to an equivalent of the mixture of a phospholipid and an optional ingredient in a ratio from about (1:1), up to about (6:1), or from about (2:1) up to about (4:1). The equivalents of the mixture are based on the combined equivalents of phospholipid based on phosphorus and equivalents of the optional ingredients. The borated phospholipids are described in European publication EP 540,700. This
10 publication is incorporated by reference.

In another embodiment, the molybdenum containing compositions may be used in combination with a mixture of (i) a borated overbased composition and (ii) an organic

polysulfide or an ashless dithiocarbamate containing composition and a phosphorus or boron antiwear/extreme pressure agent. These components are described above.

Lubricants

As previously indicated, the above combinations are useful in lubricants where they can function primarily as antiwear, antiweld, extreme pressure, anticorrosion, antioxidation and/or friction modifying agents. They can be employed in a variety of lubricants based on diverse oils of lubricating viscosity, including natural and synthetic lubricating oils and mixtures thereof. These lubricants include crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines, including automobile and truck engines, two-cycle engines, aviation piston engines, marine and railroad diesel engines, and the like. They can also be used in gas engines, stationary power engines and turbines and the like. Automatic or manual transmission fluids, transaxle lubricants, gear lubricants, including open and enclosed gear lubricants, tractor lubricants, metal-working lubricants, hydraulic fluids and other lubricating oil and grease compositions can also benefit from the incorporation therein of the compositions of the present invention. They may also be used as wire rope, walking cam, way, rock drill, chain and conveyor belt, worm gear, bearing, and rail and flange lubricants.

The combinations may be used in lubricants or in concentrates. The concentrate may contain the above combinations and/or other components used in preparing fully formulated lubricants. The concentrate also contains a substantially inert organic diluent, which includes kerosene, mineral distillates, or one or more of the oils of lubricating viscosity discussed below. The combinations are present in a final product, blend, or concentrate in any amount effective to act as an antiwear, antiweld, and/or extreme pressure agents in lubricating compositions.

In one embodiment, the lubricating composition contains up to 1.5%, or up to about 1.0%, or up to about 0.5% by weight of reaction product of a polyisobutenyl substituted succinic anhydride and a polyalkylene polyamine. In another embodiment, the lubricating compositions, such as gear lubricants, contain up to 2%, or up to 1.5%, or up to 1% by weight of a dispersant, such as those described herein. In another embodiment, the lubricating composition is free of added lead compounds, such as lead naphthanates, dithiophosphates and dithiocarbamates.

The lubricating compositions and methods of this invention employ an oil of lubricating viscosity, including natural or synthetic lubricating oils and mixtures thereof. Natural oils include animal oils, vegetable oils, mineral lubricating oils, and solvent or acid treated mineral oils. Synthetic lubricating oils include hydrocarbon oils (polyalpha-olefins), halo-substituted hydrocarbon oils, alkylene oxide polymers, esters of dicarboxylic acids and polyols, esters of phosphorus-containing acids, polymeric tetrahydrofurans and silicon-based oils. Unrefined, refined, and rerefined oils, either natural or synthetic, may be used in the compositions of the present invention. A description of oils of lubricating viscosity occurs in U.S. Patent 4,582,618 (column 2, line 37 through column 3, line 63, inclusive), herein incorporated by reference for its disclosure to oils of lubricating viscosity.

In one embodiment, the oil of lubricating viscosity is a polyalpha-olefin (PAO). Typically, the polyalpha-olefins are derived from monomers having from about 3 to about 30, or from about 4 to about 20, or from about 6 to about 16 carbon atoms. Examples of useful PAOs include those derived from decene. These PAOs may have a viscosity from about 3 to about 150, or from about 4 to about 100, or from about 4 to about 8 cSt at 100°C. Examples of PAOs include 4 cSt polyolefins, 6 cSt polyolefins, 40 cSt polyolefins and 100 cSt polyalphaolefins.

In one embodiment, the oil of lubricating viscosity are selected to provide lubricating compositions with a kinematic viscosity of at least about 3.5 cSt, or at least about 4.0 cSt at 100°C. In one embodiment, the lubricating compositions have an SAE gear viscosity grade of at least about SAE 75W. The lubricating composition may also have a so-called multigrade rating such as SAE 75W-80, 75W-90, 75W-90, 75W-140, 80W-90, 80W-140, 85W-90, or 85W-140. Multigrade lubricants may include a viscosity improver which is formulated with the oil of lubricating viscosity to provide the above lubricant grades. Useful viscosity improvers include but are not limited to polyolefins, such as ethylene-propylene copolymers, or polybutylene rubbers, including hydrogenated rubbers, such as styrene-butadiene or styrene-isoprene rubbers; or polyacrylates, including polymethacrylates. In one embodiment, the viscosity improver is a polyolefin or polymethacrylate. Viscosity improvers available commercially include Acryloid™ viscosity improvers available from Rohm & Haas; Shellvis™ rubbers available from Shell Chemical; Trilene™ polymers, such as Trilene™ CP-40, available commercially from

Uniroyal Chemical Co., and Lubrizol 3100 series and 8400 series polymers, such as Lubrizol 3174 available from The Lubrizol Corporation.

In one embodiment, the oil of lubricating viscosity includes at least one ester of a dicarboxylic acid. Typically the esters containing from about 4 to about 30, preferably from about 6 to about 24, or from about 7 to about 18 carbon atoms in each ester group. Examples of dicarboxylic acids include glutaric, adipic, pimelic, suberic, azelaic and sebacic. Examples of ester groups include hexyl, octyl, decyl, and dodecyl ester groups. The ester groups include linear as well as branched ester groups such as iso arrangements of the ester group. A particularly useful ester of a dicarboxylic acid is diisodecyl azelate.

In another embodiment, the oil of lubricating viscosity is selected to provide lubricating compositions for crankcase applications, such as for gasoline and diesel engines. Typically, the lubricating compositions are selected to provide an SAE crankcase viscosity number of 10W, 20W, or 30W lubricants. The lubricating composition may also have a so called multi-grade rating such as SAE 5W-30, 10W-30, 10W-40, 20W-50, etc. As described above, multi-grade lubricants include a viscosity improver which is formulated with the oil of lubricating viscosity to provide the above lubricant grades.

Other Additives

The invention also contemplates the use of other additives together with the above combinations. Such additives include, for example, detergents and dispersants, corrosion- and oxidation-inhibiting agents, pour point depressing agents, extreme pressure agents, antiwear agents, color stabilizers and anti-foam agents.

The detergents are exemplified by oil-soluble neutral and basic salts (i.e. overbased salts) of alkali or alkaline earth metals with sulfonic acids, carboxylic acids, phenols or organic phosphorus acids, such as those described above. The oil-soluble neutral or basic salts of alkali or alkaline earth metal salts may also be reacted with a boron compound. Boron compounds are described above. The overbased and borated overbased metal salts are described above. Examples of useful overbased and borated overbased metal salts include sodium, calcium and magnesium overbased and borated overbased sulfonates and carboxylates, including the above hydrocarbyl substituted carboxylic acylating agents.

Detergents and dispersants are known in the art. The following are illustrative.

(1) "Carboxylic dispersants" are the reaction products of carboxylic acids (or derivatives thereof) containing at least about 34 and preferably at least about 54 carbon atoms and nitrogen containing compounds (such as amines), organic hydroxy compounds (such as phenols and alcohols), and/or basic inorganic materials. These reaction products include imide, amide, and ester reaction products of carboxylic acylating agents. The carboxylic dispersants are generally prepared by reacting one or more of the above described hydrocarbyl substituted carboxylic acylating agent (described above) with an amine (described above), preferably the polyalkylenepolyamine or the condensed polyamine, or hydroxy containing compound, such as an alcohol and optionally an amine. Examples of these materials include succinimide dispersants and carboxylic ester dispersants. Examples of these "carboxylic dispersants" are described in British Patent 1,306,529 and in many U.S. Patents including the following: 3,219,666, 3,316,177, 3,340,281, 3,351,552, 3,381,022, 3,433,744, 3,444,170, 3,467,668, 3,501,405, 3,542,680, 3,576,743, 3,632,511, 4,234,435, 5,230,714 and Re 26,433.

(2) "Amine dispersants" are the reaction products of relatively high molecular weight aliphatic or alicyclic halides and amines, preferably polyalkylene polyamines. These dispersants are described above as polyalkene-substituted amines. Examples thereof are described for example, in the following U.S. Patents: 3,275,554, 3,438,757, 3,454,555, and 3,565,804.

(3) "Mannich dispersants" are the reaction products of alkylphenols and aldehydes (especially formaldehyde) and amines (especially amine condensates and polyalkylenepolyamines). The materials described in the following U.S. Patents are illustrative: 3,036,003, 3,236,770, 3,414,347, 3,448,047, 3,461,172, 3,539,633, 3,586,629, 3,591,598, 3,634,515, 3,725,480, 3,726,882, and 3,980,569.

(4) "Post-treated dispersants" are the products obtained by post-treating the carboxylic, amine or Mannich dispersants with reagents such as urea, thiourea, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles, epoxides, boron compounds, phosphorus compounds or the like. Exemplary materials of this kind are described in the following U.S. Patents: 3,200,107, 3,282,955, 3,367,943, 3,513,093, 3,639,242, 3,649,659, 3,442,808, 3,455,832, 3,579,450, 3,600,372, 3,702,757, and 3,708,422.

(5) "Polymeric dispersants" are interpolymers of oil-solubilizing monomers such as decyl methacrylate, vinyl decyl ether and high molecular weight olefins with monomers containing polar substituents, e.g., aminoalkyl acrylates or acrylamides and poly-(oxyethylene)-substituted acrylates. Polymeric dispersants include esters of styrene-maleic anhydride copolymers. Examples thereof are disclosed in the following U.S. Patents: 3,329,658, 3,449,250, 3,519,656, 3,666,730, 3,687,849, and 3,702,300.

The above-noted patents are incorporated by reference herein for their disclosures of ashless dispersants.

Auxiliary extreme pressure agents and corrosion- and oxidation-inhibiting agents which may be included in the lubricants of the invention are exemplified by chlorinated aliphatic hydrocarbons such as chlorinated waxes; sulfurized alkylphenols; phosphites including di- or trihydrocarbyl phosphites, such as dibutyl phosphite, trioctyl phosphite and triphenyl phosphite; phosphosulfurized hydrocarbons, such as the reaction product of a phosphorus sulfide with turpentine or methyl oleate; metal thiocarbamates, such as zinc dioctyldithiocarbamate, and barium diheptylphenyl dithiocarbamate. Many of the above-mentioned extreme pressure agents and corrosion- and oxidation-inhibitors also serve as antiwear agents.

Pour point depressants are an additive often included in the lubricating oils described herein. Examples of useful pour point depressants are polymethacrylates; polyacrylates; polyacrylamides; condensation products of haloparaffin waxes and aromatic compounds; vinyl carboxylate polymers; and polymers of dialkylfumarates, vinyl esters of fatty acids and alkyl vinyl ethers. Pour point depressants useful for the purposes of this invention, techniques for their preparation and their uses are described in U.S. Patents 2,387,501; 2,015,748; 2,655,479; 1,815,022; 2,191,498; 2,666,746; 2,721,877; 2,721,878; and 3,250,715 which are hereby incorporated by reference for their relevant disclosures.

Antifoam agents are used to reduce or prevent the formation of stable foam. Typical antifoam agents include silicones or organic polymers. Additional antifoam compositions are described in "Foam Control Agents", by Henry T. Kerner (Noyes Data Corporation, 1976), pages 125-162.

The following examples relate to lubricating compositions containing the combination of a dithiocarbamate compound and an organic polysulfide.

Example 1

A lubricant is prepared by incorporating 1.5% by weight of the product of Example M-1 and 1% of the product of Example B-2 into a 80W-90 gear oil base oil.

Example 2

5 A lubricating composition is prepared as described in Example 1, except a 10W-30 oil is used instead of the 80W-90 oil.

Example 3

0 A lubricating oil is prepared by incorporating 1.5% of the product of Example M-1, 2.5% of the product of Example S-1, and 1.2% by weight of the product of Example P-3 into an 80W-90 gear oil.

Example 4

A lubricating composition is prepared as described in Example 3 except a 10W-30 oil is used instead of the 80W-90 oil.

Example 5

5 A lubricating oil is prepared by incorporating 1.5% of the product of Example M-1, 1% of the product of Example B-2, 2.5% of the product of Example S-1, 1.2% of a mixed salt of isooctyl dithiophosphoric acid and 2-ethylhexanoic acid, 0.7% of dibutyl hydrogen phosphite, 1.8% of calcium overbased salt of an alkylbenzene sulfonic acid (having a metal ratio of 12, 53% diluent, comprising 100 neutral mineral oil and
0 unreacted alkylbenzene alkylate, a total base number of 30, and a 385 molecular weight for the sulfonic acid), 0.25% of oleylamide, and 0.07% of silicon antifoam agent into a 80W-90 oil.

Example 6

A lubricating compositions is prepared by incorporating 0.2% by weight of Sakura Lube 500, 3.8% by weight to the product of Example S-1, 1.3% by weight of the product of Example P-3

Example 7

The lubricating composition is prepared by incorporating 0.2% of Sakura Lube 500, 3.8% by weight of the product of Example S-1, 1.3% by weight of the product of Example P-4, 0.35% by weight of oleo amine, 0.1% by weight oleo amide, and 0.1% by weight of the reaction product of dimercaptiothiadiazole, heptylamine and paraformaldehyde into an 80W gear oil.

Example 8-12

The following table contains examples of lubricating compositions which are prepared by incorporating the ingredients into an 80W-90 gear oil.

	6	7	8	9	10	11
Example M-1	1.5	--	--	2.5	1.0	--
Sakura Lube 500	--	0.2	--	--	--	0.3
Molyvan 807	--	--	0.5	--	--	--
Example B-1	1	--	--	1.5	--	0.5
Example B-2	--	0.8	--	--	1	0.8
Example S-1	3.0	--	2.5	--	--	3.0
Example P-4	--	--	1.2	--	--	--
Example P-4	1.2	--	--	1.2	1.2	--
Phosphorus Containing ester ¹	--	1.5	--	--	--	1.5
Dithiocarbamate ester ²	--	2.5	1	--	2.5	--
Dibutyl hydrogen phosphite	0.7	--	--	--	--	1.0

1 A reaction product of isobutyl, amyl dithiophosphoric acid, methyl acrylate and propylene oxide.

2 A reaction product diethyl amine, carbon disulfide, and methyl acrylate.

While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

Claims

1. A lubricating composition comprising a major amount of an oil of lubricating viscosity and

(A) an antiwear improving amount of at least one molybdenum containing composition, and

(B) at least one member selected from the group consisting of

(i) at least one borated overbased metal salt of an acidic organic compound, provided that (A) and (Bi) are not the same,

(ii) a combination of (a) at least one organic polysulfide or at least one ashless dithiocarbamate containing composition and (b) at least one component selected from the group consisting of a metal thiophosphate, a phosphoric acid ester or salt thereof, a phosphorus-containing carboxylic acid, ester, ether, or amide, a borated dispersant, an alkali metal borate, a borated fatty amine, a borated phospholipid, a borate ester, and mixtures thereof, and

(iii) a combination of (i) and (ii).

2. The composition of claim 1, wherein (A) is present in an amount to provide from about 125 to about 900 ppm molybdenum to the lubricating composition.

3. The composition of claim 1, wherein (A) is a molybdenum containing alkali or alkaline earth metal overbased sulfonate, carboxylate, or phenate.

4. The composition of claim 1, wherein (A) is molybdenum containing alkali or alkaline earth metal sulfonate.

5. The composition of claim 4, wherein the alkali or alkaline earth metal is calcium or magnesium.

6. The composition of claim 1 wherein (A) is prepared by carbonation of a mixture comprising at least one alkali or alkaline earth metal compound, an acidic organic compound, and at least one hydrocarbon insoluble organic molybdenum complex.

7. The composition of claim 6 wherein the organic molybdenum complex is an amine molybdenum complex.

8. The composition of claim 1 wherein (A) is at least one molybdenum thiophosphate or at least one molybdenum thiocarbamate.

9. The composition of claim 1 wherein (A) is at least one molybdenum oxysulfide dithiophosphate or at least one molybdenum oxysulfide dithiocarbamate.

10. The composition of claim 1, wherein (B) is (i) and the borated overbased salt of an acidic organic compound is a borated overbased alkali or alkaline earth metal sulfonate, carboxylate or phenate.

11. The composition of claim 1 wherein (B) is (i) and the borated overbased salt of an acidic organic compound is a borated overbased sodium, calcium or magnesium sulfonate or carboxylate.

12. The composition of claim 1, wherein (B) is (i) and the lubricating composition further comprises (C) at least one sulfurized organic compound or at least one ashless dithiocarbamate containing compound, or (D) at least one phosphorus or boron extreme pressure.

13. The composition of claim 1 wherein (B) is (ii) and the organic polysulfide is a sulfurized oil, fatty acid or ester, olefin, polyolefin or mixtures thereof.

14. The composition of claim 1 wherein (B) is (ii) and the ashless dithiocarbamate containing composition (a) is prepared by reacting a dithiocarbamic acid or salt with an unsaturated compound.

15. The composition of claim 14 wherein the unsaturated compound is an acrylic ester of the formula $R^1R^2C=C(R^3)COOR^4$, wherein R^1 , R^2 , and R^3 are each independently hydrogen or a hydrocarbyl group, and R^4 is a hydrocarbyl group containing from 1 to about 24 carbon atoms.

16. The composition of claim 14 wherein the unsaturated compound is a methyl, ethyl, butyl, pentyl, or hexyl-acrylate or methacrylate.

17. The composition of claim 1 wherein the phosphoric acid ester or salt thereof (b) is a phosphoric acid ester prepared by reacting a dithiophosphoric acid with an epoxide to form an intermediate, and the intermediate is further reacted with a phosphorus acid or anhydride, or a salt of the phosphoric acid ester.

18. The composition of claim 17 wherein the dithiophosphoric acid is a dihydrocarbyl dithiophosphoric acid independently having from 1 to about 24 carbon atoms in each hydrocarbyl group.

19. The composition of claim 18 wherein the phosphoric acid ester or salt thereof is prepared by reacting the phosphoric acid ester with ammonia or an amine.

20. The composition of claim 19 wherein the amine is a tertiary aliphatic primary amine.

21. The composition of claim 1 wherein the phosphoric acid ester or salt thereof (b) is a phosphoric acid ester prepared by reacting a phosphorus acid or anhydride with at least one alcohol wherein each alcohol independently contains from about 1 to about 30 carbon atoms, or a salt of the phosphoric acid ester.

22. The composition of claim 1 wherein the phosphoric acid ester or salt thereof is a triarylphosphate.

23. The composition of claim 22 wherein the triarylphosphate is tricresylphosphate.

24. The composition of claim 12, wherein (C) is a sulfurized olefin.

25. A lubricating composition comprising a major amount of an oil of lubricating viscosity and

(A) an antiwear improving amount of at least one molybdenum containing composition, and

(B) at least one borated overbased metal salt of an acidic organic compound, provided that (A) and (B) are not the same.

26. The composition of claim 25, wherein (A) is present in an amount to provide from about 125 to about 900 ppm molybdenum to the lubricating composition.

27. The composition of claim 25, wherein (A) is a molybdenum containing alkali or alkaline earth metal overbased sulfonate, carboxylate, or phenate.

28. The composition of claim 25, wherein (A) is a molybdenum containing alkali or alkaline earth metal overbased sulfonate.

29. The composition of claim 25 wherein (A) is prepared by carbonation of a mixture comprising at least one alkali or alkaline earth metal compound, an acidic organic compound, and at least one hydrocarbon insoluble organic molybdenum complex.

30. The composition of claim 29 wherein the organic molybdenum complex is an amine molybdenum complex.

31. The composition of claim 25 wherein (A) is a molybdenum thiophosphate or a molybdenum thiocarbamate.

32. The composition of claim 25 wherein (A) is a molybdenum oxysulfide dithiophosphate or a molybdenum oxysulfide dithiocarbamate.

33. The composition of claim 25, wherein (B) the borated overbased salt of an acidic organic compound is a borated overbased alkali or alkaline earth metal sulfonate, carboxylate or phenate.

34. The composition of claim 25 wherein (B) is a borated overbased sodium, calcium, or magnesium sulfonate or carboxylate.

35. The composition of claim 25, further comprises (C) at least one organic polysulfide or at least one dithiocarbamate containing compound, or (D) at least one phosphorus or boron antiwear or extreme pressure, wherein (B) and (D) are not the same.

36. The composition of claim 35, wherein (C) is a sulfurized olefin.

37. The composition of claim 35, wherein (C) is a dithiocarbamate ester prepared by reacting a dithiocarbamic acid or salt with an unsaturated compound.

38. A lubricating composition comprising a major amount of an oil of lubricating viscosity,

(A) at least one molybdenum containing composition, and

(B) at least one combination of (a) at least one organic polysulfide or at least one ashless dithiocarbamate containing composition and (b) a component selected from the group consisting of a metal thiophosphate, a phosphoric acid ester or salt thereof, a phosphorus-containing carboxylic acid, ester, ether, or amide, a borated dispersant, an alkali metal borate, a borated fatty amine, a borated phospholipid, a borate ester, and mixtures thereof.

39. The composition of claim 38, wherein (A) is a molybdenum containing alkali or alkaline earth metal sulfonate.

40. The composition of claim 38 wherein (A) is a molybdenum thiophosphate or a molybdenum thiocarbamate.

41. The composition of claim 38 wherein (A) is a molybdenum oxysulfide dithiophosphate or a molybdenum oxysulfide dithiocarbamate.

42. A method of lubricating a transmission or a differential comprising the steps of introducing to a transmission or differential a lubricating composition comprising a major amount of an oil of lubricating viscosity and

(A) an antiwear improving amount of at least molybdenum containing composition, and

(B) at least one member selected from the group consisting of

(i) at least one borated overbased metal salt of an acidic organic compound, provided that (A) and (Bii) are not the same,

(ii) a combination of (a) at least one organic polysulfide or at least one ashless dithiocarbamate containing composition and (b) at least one component selected from the group consisting of a metal thiophosphate, a phosphoric acid ester or salt thereof, a phosphorus-containing carboxylic acid, ester, ether, or amide, a borated dispersant, an alkali metal borate, a borated fatty amine, a borated phospholipid, a borate ester, and mixtures thereof, and

(iii) a combination of (i) and (ii), and operating the differential or transmission.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/06714

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 C10M141/10 C10M141/12 C10M159/20 C10M163/00 //(C10M163/00,135:02,135:04,135:06,135:18,137:02,137:04,137:10, 139:00,159:12,159:20,159:22,159:24),C10N10:12,C10N60:14 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 6 C10M Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 447 916 (NIPPON OIL CO.) 25 September 1991 see page 5; table 1 ---	1,2, 8-11,25, 26,31-34
E	EP,A,0 677 571 (TONEN CORPORATION) 18 October 1995 see the whole document & WO,A,94 14933 (TONEN CORPORATION) ---	1,8,9, 13,38, 40-42
X	US,A,4 501 678 (T. KATAYAMA) 26 February 1985 see page 9; examples 7,10; table 1 ---	1,8,9, 38,40-42
	-/--	
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : 'A' document defining the general state of the art which is not considered to be of particular relevance 'E' earlier document but published on or after the international filing date 'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) 'O' document referring to an oral disclosure, use, exhibition or other means 'P' document published prior to the international filing date but later than the priority date claimed 'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention 'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone 'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. '&' document member of the same patent family		
Date of the actual completion of the international search 22 January 1996		Date of mailing of the international search report 12 -02- 1996
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016		Authorized officer Hilgenga, K

INTERNATIONAL SEARCH REPORT

Inter- national Application No
PCT/US 95/06714

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,94 11470 (GKN TECHNOLOGY LIMITED) 26 May 1994 see page 5; example 1 see page 8; example 4 ---	1,2,8,9, 13,22, 23,38, 40,41
A	EP,A,0 404 650 (SOCIETE NATIONALE ELF AQUITAINE) 27 December 1990 see page 7; example 3 see claims 28,29 ---	3-7, 27-30
A	EP,A,0 041 597 (VANDERBILT) 16 December 1981 see page 2, line 5 - line 31 see page 4, line 31 ---	1,2,8,9, 13-16
A	EP,A,0 604 232 (THE LUBRIZOL CORPORATION) 29 June 1994 see page 2, line 31 - line 32 see page 10, line 5 - line 37; example P1 see page 12; examples P3-P5 see page 14, line 38 - line 58 see page 19; example IX ---	1,10-12, 17-25, 33-37
A	EP,A,0 638 631 (THE LUBRIZOL CORPORATION) 15 February 1995 -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 95/06714

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-447916	25-09-91	JP-A- 3269094 DE-D- 69102172 DE-T- 69102172	29-11-91 07-07-94 22-09-94
EP-A-677571	18-10-95	JP-A- 6200270 AU-B- 5717294 CA-A- 2151582 WO-A- 9414933	19-07-94 19-07-94 07-07-94 07-07-94
US-A-4501678	26-02-85	JP-C- 1682547 JP-B- 3031760 JP-A- 59011397	31-07-92 08-05-91 20-01-84
WO-A-9411470	26-05-94	EP-A- 0668900 GB-A- 2287715	30-08-95 27-09-95
EP-A-404650	27-12-90	FR-A- 2648473 DE-D- 69004163 DE-T- 69004163 ES-T- 2060977 JP-A- 3035094 US-A- 5143633	21-12-90 02-12-93 11-05-94 01-12-94 15-02-91 01-09-92
EP-A-41597	16-12-81	US-A- 4360438 JP-C- 1637648 JP-B- 3002919 JP-A- 57023693	23-11-82 31-01-92 17-01-91 06-02-82
EP-A-604232	29-06-94	AU-B- 5250493 CA-A- 2112183 JP-A- 6228582 US-A- 5464548	07-07-94 25-06-94 16-08-94 07-11-95
EP-A-638631	15-02-95	AU-B- 6877094 CA-A- 2129168 JP-A- 7150167	16-02-95 05-02-95 13-06-95